U.S. DEPARTMENT OF COMMERCE
National Technical Information Service

PB-273 018

# Methodology and Instrumentation to Measure Gaseous Ammonia

Monsanto Research Corp, Dayton, Ohio Dayton Lab

Prepared for

Environmental Sciences Research Lab, Research Triangle Park, N C

Aug 77

EPA-600/2-77-125
August 1977

PB 273 018

Environmental Protection Technology Series

REPRODUCED BY
NATIONAL TECHNICAL
INFORMATION SERVICE
U. S. DEPARTMENT OF COMMERCE
SPRINGFIELD, VA. 22161

## RESEARCH REPORTING SERIES

Research reports of the Office of Research and Development, U S. Environmental Protection Agency have been grouped into nine series. These nine broad categories were established to facilitate further development and application of environmental technology. Elimination of traditional grouping was consciously planned to foster technology transfer and a maximum interface in related fields. The nine series are:

1. Environmental Health Effects Research
2. Environmental Protection Technology
3. Ecological Research
4. Environmental Monitoring
5. Socioeconomic Environmental Studies
6. Scientific and Technical Assessment Reports (STAR)
7. Interagency Energy-Environment Research and Development
8. "Special" Reports
9. Miscellaneous Reports

This report has been assigned to the ENVIRONMENTAL PROTECTION TECHNOLOGY series. This series describes research performed to develop and demonstrate instrumentation, equipment, and methodology to repair or prevent environmental degradation from point and non-point sources of pollution. This work provides the new or improved technology required for the control and treatment of pollution sources to meet environmental quality standards.

This document is available to the public through the National Technical Information Service, Springfield, Virginia 22161.

**TECHNICAL REPORT DATA**
*(Please read Instructions on the reverse before completing)*

| | |
|---|---|
| 1. REPORT NO. EPA-600/2-77-125 | 2. |
| 3. RECIPIENT'S ACCESSION NO. PB275018 | |
| 4. TITLE AND SUBTITLE METHODOLOGY AND INSTRUMENTATION TO MEASURE GASEOUS AMMONIA | 5. REPORT DATE August 1977 |
| | 6. PERFORMING ORGANIZATION CODE |
| 7. AUTHOR(S) D. David, D. Ruffin and M. Willson | 8. PERFORMING ORGANIZATION REPORT NO. |
| 9. PERFORMING ORGANIZATION NAME AND ADDRESS Monsanto Research Corporation Dayton Laboratory 1515 Nicholas Road Dayton, Ohio | 10. PROGRAM ELEMENT NO. 1AD712 BE-11 (FY-77) |
| | 11. CONTRACT/GRANT NO. 68-02-1793 |
| 12. SPONSORING AGENCY NAME AND ADDRESS Environmental Sciences Research Laboratory - RTP, NC Office of Research and Development U.S. Environmental Protection Agency Research Triangle Park, N.C. 27711 | 13. TYPE OF REPORT AND PERIOD COVERED Final |
| | 14. SPONSORING AGENCY CODE EPA/600/09 |
| 15. SUPPLEMENTARY NOTES | |

16. ABSTRACT

Methodology for the time integrated collection and analysis of atmospheric ammonia was developed. Ammonia is primarily measured because it can react with $SO_x$ to produce ammonium sulfate. Since $SO_x$ is one of the principle air pollutants, it is important to determine its atmospheric reactions.

The methodology makes use of optical wave guides which are 1 x 20 mm quartz rods coated with a chemical that is specific for $NH_3$. As ammonia reacts with the chemical on the rod, the optical properties of light passing through the rod change and can be directly related to the $NH_3$ concentration. An optical wave guide analyzer was developed to measure the resulting change in optical properties. Concentrations as low as 1 ppb can be assayed. The coated quartz rods are placed in the field for 24 hours and brought back to the laboratory for analysis by the analyzer.

17. KEY WORDS AND DOCUMENT ANALYSIS

| a. DESCRIPTORS | b. IDENTIFIERS/OPEN ENDED TERMS | c. COSATI Field/Group |
|---|---|---|
| *Air Pollution | | 13B |
| *Ammonia | | 07B |
| Measurement | | 14B |
| Development | | 08G |
| *Analyzers | | 20F |
| Quartz | | |
| Optical Properties | | |

| | | |
|---|---|---|
| 18. DISTRIBUTION STATEMENT RELEASE TO PUBLIC | 19. SECURITY CLASS (This Report) UNCLASSIFIED | 21. NO. OF PAGES 117 |
| | 20. SECURITY CLASS (This page) UNCLASSIFIED | 22. PRICE A06 - A01 |

EPA Form 2220-1 (9-73)

EPA-600/2-77-125
August 1977

# METHODOLOGY AND INSTRUMENTATION TO MEASURE GASEOUS AMMONIA

by

D.J. David
M.C. Willson
D.S. Ruffin

Monsanto Research Corporation
Dayton Laboratory
Dayton, Ohio 45407

Contract Number 68-02-1793

Project Officer
James Mulik
Atmospheric Chemistry and Physics Division
Environmental Sciences Research Laboratory
Research Triangle Park, North Carolina 27711

ENVIRONMENTAL SCIENCES RESEARCH LABORATORY
OFFICE OF RESEARCH AND DEVELOPMENT
U.S. ENVIRONMENTAL PROTECTION AGENCY
RESEARCH TRIANGLE PARK, NORTH CAROLINA 27711

## DISCLAIMER

This report has been reviewed by the Environmental Science Research Laboratory, U.S. Environmental Protection Agency, and approved for publication. Approval does not signify that the contents necessarily reflect the views and policies of the U.S. Environmental Protection Agency, nor does mention of trade names or commercial products constitute endorsement or recommendation for use.

## ABSTRACT

Methodology for the time integrated collection and analysis of atmospheric ammonia was developed. Ammonia is primarily measured because it can react with $SO_x$ to produce ammonium sulfate. Since $SO_x$ is one of the principle air pollutants, it is important to determine its atmospheric reactions.

The methodology makes use of optical wave guides which are 1 x 20 mm quartz rods coated with a chemical that is specific for $NH_3$ concentration. An optical wave guide analyzer was developed to measure the resulting change in optical properties. Concentrations as low as 1 ppb can be assayed. The coated quartz rods are placed in the field for approximately 24 hours and brought back to the laboratory for analysis by the analyzer.

CONTENTS


Abstract . . . . . iii

Figures . . . . . vii

Tables . . . . . x

1. Introduction . . . . . 1

2. Concept and Theoretical Model . . . . . 3

2.1 Optical Waveguide Theory . . . . . 4

2.2 Optics of the Coating . . . . . 9

3. Instrumentation . . . . . 10

4. Experimental . . . . . 19

4.1 Survey and Selection of Ammonia Reactions. . 19

4.2 Analytical Reaction Screening . . . . . 22

4.3 Coating Studies . . . . . 25

4.4 Exposure to Ammonia of Polymer/Reagent Coatings on Waveguides . . . . . 39

4.5 Exposure to Ammonia of Polymer/Reagent Coatings on Quartz Waveguides to Determine Effect of Gas Stream Velocity. . . . . 42

4.6 Sensitivity and Dynamic Range of Collector/ Sensors and Effect of Relative Humidity. . . 46

4.6.1 Effect on Sensitivity of Coating Polymer Type . . . . . 49

4.6.2 Effect of Ammonia Concentration on Collector/Sensor Response . . . . . 52

4.7 Stability of Collector/Sensors . . . . . 57

4.8 Effect of Rod Length on Collector/ Sensor Sensitivity . . . . . 65

4.9 Effect of Acid Pollutants and Ammonium Compounds on Collector/Sensor Response . . . 68

4.10 Effect of Temperature on Collector/ Sensor Response . . . . . 72

4.11 Absorption Wavelength. . . . . 75


Preceding page blank

5. Calibration . . . . . 77

6. Results and Discussions . . . . . 79

6.1 Ambient Air Measurement of Ammonia in the Laboratory Using an Artificial Humidity Chamber . . . . . 79

6.2 Field Test Results . . . . . 83

7. Procedures . . . . . 95

7.1 Solution Preparation . . . . . 95

7.2 Rod Coating . . . . . 96

7.3 Analytical Results . . . . . 98

7.3.1 Collector Sensor Exposure and Calculations . . 98

References . . . . . 100

FIGURES


| Number | | Page |
|---|---|---|
| 1 | Light path in collector/sensor waveguide and associated optics | 5 |
| 2 | Collector/sensor model. | 7 |
| 3 | Block diagram of the gradient light analytical detector (G L A D) | 14 |
| 4 | Gradient light analytical detector (G L A D I) | 16 |
| 5 | Rotating drum waveguide coating apparatus | 27 |
| 6 | Rod holder for dip coating with beaker of polymer solution | 33 |
| 7 | The effect of high humidity and/or concentrated $NH_4OH$ on the transmission properties of PVA/ reagent coated rods | 41 |
| 8 | The effect of both low and high humidity on PVA/ninhydrin coated rods exposed to 0 & 1 ppm ammonia concentrations in an air stream | 43 |
| 9 | Schematic of equipment used to expose collector/ sensors to known concentrations of ammonia in air | 44 |
| 10 | Transmittance of 3 cm long collector/sensors as a function of exposure time and air stream velocity. | 45 |
| 11 | Hygroscopicity of various polymers. | 47 |
| 12 | Effects of relative humdity on collector/ sensor sensitivity to ammonia | 48 |
| 13 | Schematic of equipment used to expose collector/sensors to known concentrations of ammonia in air | 50 |
| 14 | The effect of polymer coating type on collector/sensor response using ninhydrin reagent | 51 |

| Number | | Page |
|---|---|---|
| 15 | The sensitivity of PVP/ninhydrin collector/ sensors at different ammonia concentrations in air | 53 |
| 16 | The sensitivity of PVA/ninhydrin collector/ sensors at different ammonia concentration in air | 54 |
| 17 | The effect of relative humidity on collector/ sensor response at a fixed concentration of ammonia in air | 55 |
| 18 | The effect of relative humidity on PVP/ ninhydrin collector/sensor response at two ammonia concentrations in air | 56 |
| 19 | The slope of PVP/ninhydrin collector/ sensor transmittance curves as a function of ammonia concentration in air | 58 |
| 20 | Effect of rod length on the transmission properties of coated rods exposed to 1 PPM ammonia in a saturated air stream. | 66 |
| 21 | The effect of high humidity and/or ammonia concentration on 4 cm long PVA ninhydrin coated rods exposed to 0 & 1 ppm ammonia in an air stream | 67 |
| 22 | Schematic of apparatus used to simultaneously expose collector/sensors to acid pollutants and ammonia | 69 |
| 23 | Effects of both acid pollutants and ammonia on the transmittance of PVP/ninhydrin coated quartz rods | 70 |
| 24 | Schematic of apparatus used to expose collector/sensors to ammonia at various temperatures | 73 |
| 25 | Effect of temperature and relative humidity on collector/sensors at 60 PPB ammonia level. | 74 |
| 26 | Absorption characteristics of reacted collector/sensors | 76 |
| 27 | Effect of both ammonia concentration and exposure time on c/s absorbance | 78 |

| Number | | Page |
|---|---|---|
| 28 | Artificial humidity chamber . . . . . | 80 |
| 29 | Modified G L A D collector/sensor holder. . . . . | 84 |
| 30 | Holder in position under roof of high volume sampler . . . . . | 88 |

TABLES


| Number | | Page |
|---|---|---|
| 1 | Transmission Measurements of an Uncoated Quartz Rod Using GLAD | 17 |
| 2 | Colorimetric Ammonia Reactions | 20 |
| 3 | Analytical Reagent/Reaction Requirements for EPA Ammonia Collector/Sensors | 22 |
| 4 | Laboratory Evaluation of Ammonia Reactions | 24 |
| 5 | Process Conditions and Coating Properties of Polymer/Reagent Coatings on Quartz Waveguides (Rods) | 28 |
| 6 | Variation of Polymer/Reagent Coating Thickness and Weight | 30 |
| 7 | Coating Thickness and Weight Reproducibility of PVA/Ninhydrin Coatings Made Using Rotating Drum Method | 31 |
| 8 | Process Conditions and Coating Properties For Rods Coated Using Vertical Axis Method | 35 |
| 9 | Comparison of Coating Methods | 36 |
| 10 | Coating Thickness and Weight Reproducibility of PVA/Ninhydrin Coatings made Using Vertical Axis Method | 38 |
| 11 | Process Conditions and Coating Properties for Rods Coated with a Number of Different Polymers and Polymer Combinations | 40 |
| 12 | Stability of Polymer/Ninhydrin Coated Collector/Sensors | 59 |
| 13 | Long Term Stability of PVA/Ninhydrin Coated Collector Sensors | 61 |
| 14 | Long Term Stability of PVA/Ninhydrin Coated Collector/Sensors | 62 |

| Number | | Page |
|---|---|---|
| 15 | Stability Comparison of Polymer/Ninhydrin Coated Collector/Sensors Stored at Ambient and Sub-Ambient Temperatures . . . . . | 64 |
| 16 | Exposure Conditions and Results of Collector/Sensors Exposed to Ambient Air in the Laboratory . . . . . | 82 |
| 17 | Analytical Results of 1st MRC Dayton Laboratory Field Site Testing. . . . . | 87 |
| 18 | Analytical Results of St. Louis Field Site Testing at EPA Regional Air Pollution Site #108 in Vicinity of Granite City, Illinois . . . . . | 92 |
| 19 | Analytical Results of 2nd MRC Dayton Laboratory Field Site Testing Using Improved Holder and PVA/PVP Coating. . . . . | 92 |

## SECTION 1

## INTRODUCTION

One of the goals of the Environmental Protection Agency (EPA) is to accurately monitor the concentration of ammonia in ambient air. The concentrating range of interest is 4 to 400 $\mu g/m^3$ (≈ 5-500 ppb) for ammonia and 0.04 $\mu g/m^3$ for particulate. Thus, a sensitive specific method of analysis is required, especially for the lower end of the concentration ranges. Measurements in this range are needed to allow detection and measurement of background concentrations of about 6 $\mu g/m^3$.[1]

Man contributes a comparatively small portion of ammonia and the major increases or decreases in ambient air are probably due to naturally occurring atmospheric phenomena in which nitrogen species are created, converted, or removed.

At the present time, monitoring is generally accomplished by periodic measurements with devices such as the midget impinger or sophisticated, expensive instruments such as the long path infrared or chemiluminescent analyzers. Each approach has its own inherent limitations. Midget liquid impingers use bulky

---

[1]Sittig, Marshall, Pollution Detection and Measuring Handbook, Park Ridge, N. J., Noyes Data Corp. (1974).

and cumbersome solution techniques for collection and require long collection times (100-1000 hours) to achieve the desired sensitivity. The use of real-time instrumentation (which is complex and expensive) in the field is useful since it provides the peak concentrations but unfortunately does not give time weighted average concentrations. In addition, this latter approach is not amenable to large scale surveillance.

The purpose of this program, therefore, was to develop practical instrumentation and methods for detecting and determining ambient air concentrations of ammonia in gaseous and particulate form.

## SECTION 2

## CONCEPT AND THEORETICAL MODEL

The prime prerequisites for any collection/analysis technique are inherent sensitivity and specificity to fulfill quantitative analysis requirements. Thus, other components of polluted air must not interfere to the extent that erroneous measurement results are obtained. Secondarily, the technique should be relatively simple and not require expensive and complex analytical instrumentation. Only if both these criteria are met can the technique be expected to gain wide acceptance and provide the large scale analytical results desired by the EPA. In addition to the direct application of the technique for the collection and analysis of ammonia it is highly desirable that the technique have wider and more general applicability in the determination of other air pollutants.

The concept we chose in order to accomplish the goals of this program is based on a new technique and instrumentation[2] that utilizes coated optical waveguides for the spectrophotometric measurement of chemical reactions carried out *in situ* on the coated surface of the waveguide. The high sensitivity

[2]Hardy, E. E., David, D. J., Kapany, N. S. and Unterleitner, F. C., Nature 257, 666 (1976).

demonstrated, the small size, the simplicity, and the low cost of the sensitized waveguides and instrumentation appeared to make this technique ideal for large scale ambient air monitoring.

The basic approach is to sensitize a waveguide to selectively react with ammonia by incorporating a reactive chemical into a passive coating on the surface of the waveguide and then placing the sensitized waveguide at desired field locations for reaction. If the reaction brings about a color change or light scattering, the change in light transmission (T) through the coating can be measured spectrophotometrically. A simplified model of the system is shown in Figure 1, i.e., light source, waveguide, and detector.

## 2.1 OPTICAL WAVEGUIDE THEORY

Although the general optical mechanisms have been considered previously,[2] we felt that it was necessary to examine a model in detail in order to define those physical parameters that would influence sensitivity dynamic range, and analytical accuracy. The question of sensitivity is of particular importance in the case of the determination of low levels of pollutants in ambient air.

## LIGHT PATH IN COLLECTOR/SENSOR WAVEGUIDE

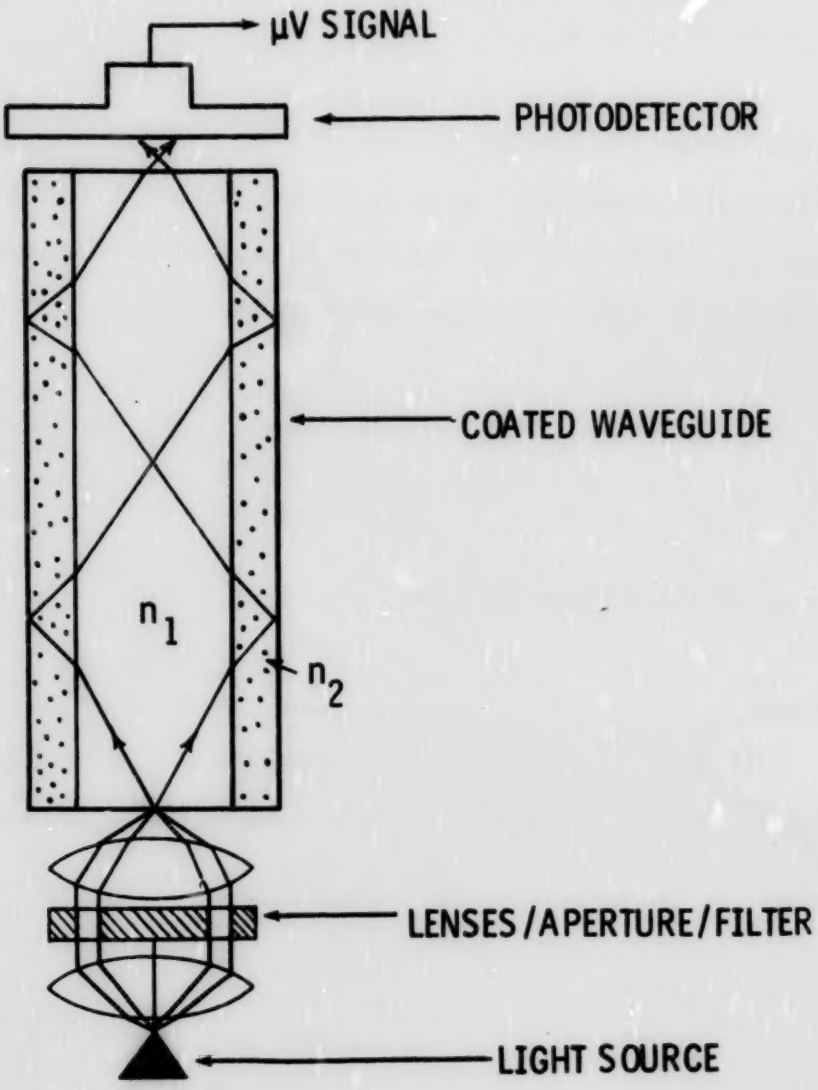



Figure 1. Light path in collector/sensor waveguide and associated optics

Accordingly, the model shown in Figure 2 was considered.[3] This model consists of a quartz rod of refractive index $n_1$ coated with a polymer containing reactants for a material of refractive index $n_2$ and light entering the rod from a medium (air) of refractive index $n_0$.

Thus, when the coated quartz rod is functioning as a waveguide, light impinging on the polymer/air interface at angles greater than $\phi_2$ is internally reflected, and light impinging on the polymer/air interface at angles less than $\phi_2$ is lost.

$$\text{for } \phi_2 = 42°$$
$$\psi_2 = 48°$$

From Snell's Laws we have

$$n_1 \sin\phi_1 = n_2 \sin\phi_2$$
$$\sin\phi_1 = \frac{1.5}{1.48} \sin 42°$$
$$\phi_1 = 43°$$
$$\therefore \psi_1 = 47°$$

$$n_0 \sin\theta_1 = n_1 \sin\psi_1$$
$$\sin\theta_1 = \frac{1.48}{1} \sin 47°$$
$$= 1.08$$

[3]David, D. J., Willson, M. C., and Ruffin, D. S., Analytical Letters, 9(4), 389 (1976).

Figure 2. Collector/sensor model

$\phi_2$ = critical angle, where $\sin \phi_2 = \frac{n_0}{n_2}$ for a critical situation

$n_0$ = refractive index of air = 1.0

$n_1$ = refractive index of quartz = 1.48

$n_0$ = refractive index of polymer matrix = 1.50

$\sin \phi_2 = \frac{1}{1.50}$ ; $\phi_2 = 42°$

$\phi_3$ = critical angle, where $\sin \phi_3 = \frac{n_1}{n_2}$ for a critical situation

$x$ = coating thickness

$\theta_1$ = acceptance angle or rod or angle of incidence

$\psi_1$ = angle of refraction in rod

$\phi_1$ = critical angle where $\sin \phi_1 = \frac{n_2}{n_1}$ for a critical situation

$\theta_2 = \psi_1$ = acceptance angle of polymer matrix and reactants or angle of incidence

$\psi_2$ = angle of refraction in polymer matrix

Further, this result shows that light at all angles is accepted and that even light entering at 90° will be internally reflected in the waveguide. In practace a hollow cone of light will be instrumentally allowed to enter the end of the rod at steep angles (≈70°-80°) by means of an appropriate aperture in order that the maximum and consistent path length through the reactive coating is followed as nearly as possible by all light rays.

However, some of the light entering the coating will be transmitted through the coating as such and will not reenter the rod. This is dictated by $\phi_3$ which is the critical angle which determines whether or not internal reflection occurs in the polymer and is defined by

$$\sin\phi_3 = \frac{n_1}{n_2} = \phi_3 = 81°$$

Since light will normally impinge on the polymer glass interface at angles less than the critical angle or angles about 42°, it will not be internally reflected within the polymer coating. This effect depends on the spread of angles of the hollow cone of light and whether or not scattered light at very low angles of incidence is able to enter the rod. This aspect is controlled instrumentally.

The number of reflections through a waveguide is given by

$$n_m = \frac{\sin\theta}{d(n_1^2-\sin^2\theta)}$$

where $\theta$ = acceptance or incidence angle

$d$ = diameter

$n_1$ = refractive index of waveguide

For a 0.1 cm rod 2 cm long, $n_m = 12$

Assuming a coating thickness of ~0.01 cm, which is borne out by actual measurement, we have for the path length

$$\sin 48° = \frac{x}{l}$$

$$l = \frac{0.01}{\sin 48°} = 0.0135 \text{ cm}$$

The total path length = l total = 0.0135 x 2 x 12 = 0.32 cm

## 2.2 OPTICS OF THE COATING

There appear to be three mechanisms which control the interaction of a gaseous pollutant with the collector/sensor and its ability to be measured:

(1) The amount of sample contacting the polymer matrix layer

(2) The diffusion of the active component through the polymer matrix layer; and

(3) The light absorption of the reaction products in accordance with Beer's Law

The change in concentration with respect to time can be formally

expressed as:

$$\frac{dC_p}{dt} = C_G \times E_G$$

where $C_p$ = concentration of pollutant vapor in polymer

$C_G$ = concentration of pollutant in gas or air

$E_G$ = extraction coefficient of polymer/polymer reactants.

$E_G$ is determined by the diffusion of the active sample component through the polymer film and the reactants ability to effectively capture it after the component has contacted the polymer matrix. Under simplified conditions, where both $E_G$ and $C_G$ (mass transfer from the air not limiting) are constant, we have

$$C_p = C_G \times E_G \ (t_2 - t_1)$$

From previous experiments, we utilized data at which the response to a known concentration of gaseous HCN over a specified time interval was the same as when a known concentration of NaCN was applied to the rod which allows an estimation of $E_G$, assuming similar thicknesses of layers and extraction coefficients.

The absorption coefficient $k_1$ from Beer's Law, $T = I/I_0 = e^{-kcl}$, was estimated in a similar manner. Assuming a similar response for $NH_3$ and a time span of 48 hours allowed estimation of

$C_{P(NH_3)}$ contained in the volume element, V = $\pi$xdl. This concentration in g/cm was substituted in Beer's Law equation equation which showed that a measurable absorbance could be obtained at the desired lower concentration limit.

The model also illustrated that the C/S operates as a concentration-sensitive detector as opposed to a mass-sensitive detector.[4,5] Since flow does not appear in the equation, the device should be essentially flow insensitive and it should not be necessary to monitor flow or attempt to pump air over the C/S.

The extraction or partition coefficient ($E_G$) addresses the removal of $NH_3$ from the air only on a gross basis since, in addition to removal, the diffusion of the $NH_3$ through the polymer coating and the rate of reaction of the $NH_3$ with the reactant in the polymer are involved in producing the reaction product. The diffusion of the $NH_3$ into the polymer coating and mass transfer to the ninhydrin, which maintains a low or zero concentration gradient by formation of irreversible colored reaction products, may well be the reaction limiting steps, as opposed to the velocity with which the sample is brought to the C/S.

---

[4]Halasz, I. Anal. Chem. 36, 1428 (1964).

[5]David, D. J., "Gas Chromatographic Detectors", Wiley-Interscience, New York (1974).

These aspects hopfully provide guidance in exercising control over those factors primarily responsible for sensitivity and quantative response and how they might be manipulated to provide the desired result.

## SECTION 3

## INSTRUMENTATION

To measure the response of the collector/sensors, suitable instrumentation was fabricated. Similar instrumentation has been described previously.

A model of the basic elements of this instrumentation and its use with a reactant coated waveguide is shown in Figure 1. These elements consist of a light source, collimating lens, aperture to produce the hollow cone of light, a lens to focus the cone on the end of the coated waveguide, and a photodetector that measures the axially transmitted light. The instrument into which these elements have been incorporated is termed a Gradient Light Analytical Detector (GLAD). This instrument will accommodate rods 0.9 - 1.3 mm in diameter and either 10 or 20 mm long. A schematic diagram showing the basic optical design is shown in Figure 3. Three filters are available which allow the selection of white, red, blue, and green light. After multiple reflections within the rod, the light from a tungsten lamp emerges at the upper face and is scattered by a diffuser, part of the light going into a silicon photodiode detector. An

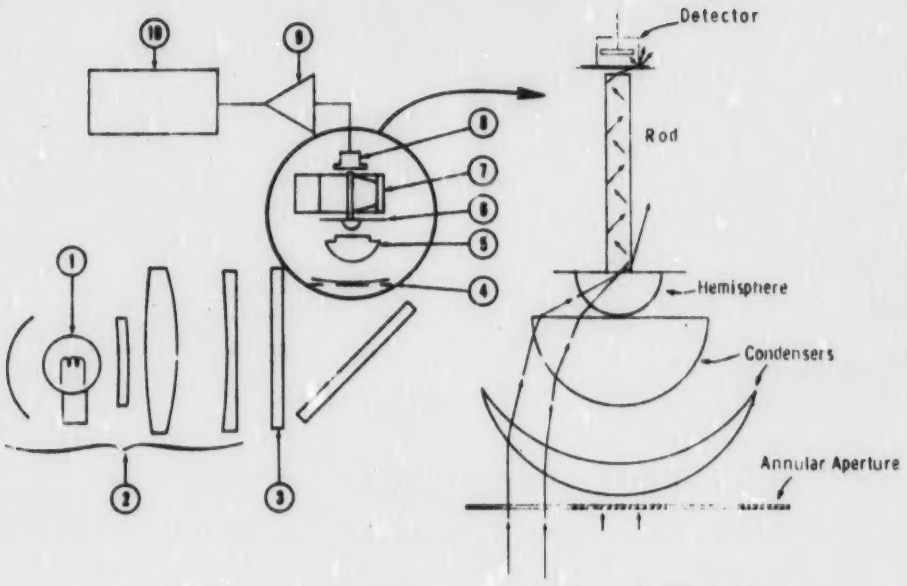



Figure 3. Block diagram of the gradient light analytical detector (GLAD)

(1) a tungsten filament lamp light source

(2) a condenser system to produce nearly collimated light

(3) a filter for wavelength selection

(4) an annular aperture to block axial light rays

(5) a condenser to produce a hollow cone of light rays

(6) coupling hemispheres and apertures to couple large angle rays into the rod

(7) a rod mount to accurately position rods with respect to the aperture while presenting a minimum of surface contact

(8) a silicon photidiode detector

(9) an operational amplifier operating as "current-to-voltage" converter

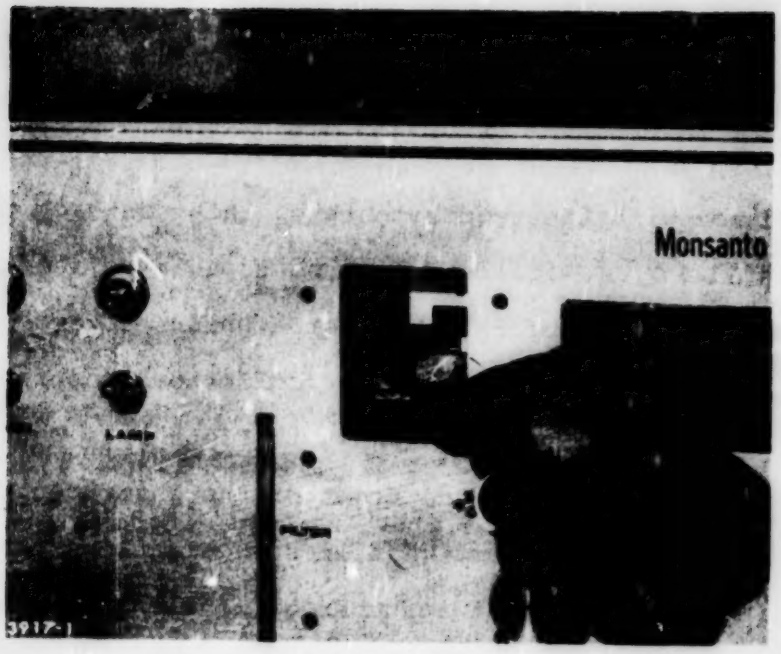
(10) a three-digit voltmeter for relative transmittance readout

output voltage suitable for the 200 mv full scale digital panel meter is selected by a decade range switch. The actual instrument is shown in Figure 4.

In order to separate inherent instrument variations from coating process variations a single uncoated quartz rod was selected and measured over a period of several weeks and at different times during the day. Two readings were taken at any one time and an average of these two was used. The procedure used for all transmittance measurements was to turn the rod end for end after the first reading. The results of this study are shown in Table 1. The percent variance is very minimal in the case of green light and thus ensures meaningful transmission measurements.

In accordance with the requirements of this contract this instrument (G L A D I) will be delivered capable of measuring the light transmittance before and after exposure to ammonia of polymer/reagent coated quartz rods (collector/sensors). The instrument to be delivered is shown in Figure 4. The collector sensors are inserted into the front of the instrument and form part of the optical system. A filter wheel allows the transmittance to be measured at a number of wavelengths. A special interference filter has been installed which will provide measurements at 580 nm ± 10 nm. This is at or near the wavelength where maximum absorption due to the ninhydrin-ammonia

(a) Overall view




(b) Inserting collector/sensor

Figure 4. Gradient light analytical detector (G L A D I)

TABLE 1. TRANSMISSION MEASUREMENTS OF AN UNCOATED QUARTZ ROD USING GLAD

| Date (1975) | Trial (X) | White Light, millivolts | Green Light, millivolts |
|---|---|---|---|
| 7/9 | 1 | 128.5 | .745 |
| 7/15 | 2 | 122.2 | .715 |
| 7/17 | 3 | 1[illegible]2.[illegible] | .715 |
| 7/18 | 4 | 128.4 | .744 |
| 7/21 | 5 | 134.6 | .778 |
| 7/22 | 6 | 127.6 | .742 |
| 7/22 | 7 | 129.7 | .744 |
| 7/23 | 8 | 128.1 | .727 |
| 7/23 | 9 | 132.5 | .774 |
| 7/23 | 10 | 131.5 | .750 |
| 7/24 | 11 | 128.0 | .728 |
| 7/24 | 12 | 131.4 | .760 |
| 7/25 | 13 | 126.8 | .718 |
| 7/31 | 14 | 127.2 | .728 |
| 8/1 | 15 | 121.9 | .696 |
| 8/4 | 16 | 125.1 | .718 |
| Average ($\bar{X}$) | | 127.9 | .736 |
| Variance | | 13.2 | .033 |
| Percent Variance | | ±5.2 | ±2.2 |

$$\text{Variance} = \sqrt{\frac{\Sigma X_i^2 - n\bar{X}^2}{n-1}} \quad \text{where } n = 16$$

reaction takes place.

A more advanced, feasible, version of this instrument was designed and developed in house. This instrument, G L A D II, was also used during this program as a supplement to G L A D I. This versatile instrument allows a broader selection of filters and light entry angles along with greater sensitivity.

# SECTION 4

# EXPERIMENTAL

## 4.1 SURVEY AND SELECTION OF AMMONIA REACTIONS

A library literature search was conducted in an effort to find analytical ammonia reactions with emphasis on colorimetric ones. Typical sources were books on analytical reagents and spot test methods. Also, the chemical abstracts were searched from the present back to 1925. A computer search of the chemical abstracts to 1972 was also made and proved particularly helpful. Pertinent information sources are listed in literature cited.[6-70]

Table 2 shows a tabulation of those reactions which looked promising. An analysis of these reactions according to the characteristics shown in Table 2 was then made. Out of a total of thirty-eight potential reactions, eighteen were selected for further study. The status of each reaction is also shown. In most cases, a reaction was disqualified prior to screening if the stability of the reagents or reaction products was judged to be poor.

At the outset of this work we felt that the reactant coating formulation must meet a number of system requirements. Consideration of possible reactants, the process of selection, and the

[6-70] See Reference Cited

TABLE 2. COLORIMETRIC AMMONIA REACTIONS

| Reagent/Reactant | Sensitivity, micrograms | Specificity | Color | Estimated Stability: Reagent | Estimated Stability: Reaction Products | Remarks | Status | Reference |
|---|---|---|---|---|---|---|---|---|
| Alloxantine in Acetic Acid | N.G. | N.G. | N.G. | Good | Good | | Has been evaluated | 49 |
| O-Benzenesulfonamido-p-benzoquinone | N.G. | N.G. | Blue | Good | Good | | Will be evaluated | 48 |
| Bromocresol Green | N.G. | N.G. | Green | Poor | Poor | Reagent is unstable | Will not be evaluated | 65 |
| Calcium Sulfate | N.G. | N.G. | N.G. | Good | Good | | Has been evaluated | 1 |
| Chloroplatinic acid | 100 | Sensitive to volatile amines | Yellow | Good | Good | Insufficient Sensitivity | Will not be evaluated | 25 |
| Cupric Chloride & Chromotropic Acid | N.G. | N.G. | Purple-Red | Fair | Fair | | Will be evaluated | 63 |
| Cuprous Chloride & Manganese Nitrate | N.G. | N.G. | Dark Brown | Good | Good | | Has been evaluated | 1 |
| Cuprous Chloride & Tannic Acid | N.G. | N.G. | Dark Brown | Fair | Fair | | Has been evaluated | 1 |
| Diamino phenol | 0.3 | N.G. | Yellow | Fair | Fair | | Will be evaluated | 19 |
| Diazotized Benzidene | .015* | N.G. | N.G. | Poor | Poor | Reagents are carcinogens | Will not be evaluated | 5 |
| Diazotized α-Naphthylamine | 0.1* | N.G. | N.G. | Poor | Poor | Reagents are carcinogens | Will not be evaluated | 6 |
| Diazotized β-Naphthylamine | 0.018* | N.G. | Orange | Poor | Poor | Reagents are carcinogens | Will not be evaluated | 7 |
| Diazotized p-Nitroaniline | N.G. | N.G. | N.G. | Poor | Poor | Very unstable | Will not be evaluated | 8 |
| Diazotized p-Phenylenediamine | <1** | Sensitive to hydrogen sulfide | N.G. | Poor | Poor | Very unstable | Will not be evaluated | 9 |
| Diazotized Sulfanilic Acid | <1** | N.G. | N.G. | Poor | Poor | Very unstable | Will not be evaluated | 10 |
| Ferric Sulfate | Good | Good | Violet | Good | Good | | Has been evaluated | 1 |
| Glutamic Dehydrogenase | <1 | Good | N.G. | Poor | Good | | Reagent is unstable | 55 |
| Manganese Sulfate & Hydrogen Peroxide | 0.03 | N.G. | Blue | Fair | Fair | | Will not be evaluated | 14 |
| Manganese Sulfate & Silver Nitrate | .05 | N.G. | Black or Silver | Fair | Fair | Photosensitive | Will not be evaluated | 11, 60 |
| Mercurous Chloride | 100 | Sensitive to organic amines | Black | Fair | Fair | Reagents are Unstable | Will not be evaluated | 24 |
| Phenol & Chloramine T | 40 | Good | Blue | Fair | Fair | | Will be evaluated | 57 |
| Phenol & Sodium Hypochlorite (Berthelot's Reaction) | 0.1 | Sensitive to aromatic amines | Blue | Fair | Fair | | Has been evaluated | 16,27,33,36, 38,39,40,41 42,49,50,58 61 |

Continued

Table 2. (Continued)

| Reagent/Reactant | Sensitivity, micrograms | Specificity | Color | Estimated Stability: Reagent | Reaction Products | Remarks | Status | Reference |
|---|---|---|---|---|---|---|---|---|
| Phenol & Sodium Nitroprusside | 2 | Good | Blue | Good | Good | - | Will be evaluated | 56 |
| Ninhydrin | 0.9 | Sensitive to volatile amines | Blue | Good | Good | | Has been evaluated | 28 |
| Picric Acid, Ethyl Malonate, Alcohol & 5% Glycerol | 100 | Sensitive to potassium | Yellow (chrystal) | Poor | Poor | Reagents are volatile | Will not be evaluated | 4,15 |
| Potassium Mercuri Iodide (Nessler's Reagent) | 0.05 | Sensitive to $Hg$, $Cd$ $Hg$, $SO_4^{-2}$ | Yellow or Orange-Red | Poor | Poor | Iodine color fades rapidly | Will not be evaluated | 13,37,51 52,59 |
| Potassium Thiocyanate & Ferric Alum* | N.G. | N.G. | N.G. | Good | Good | | Will be evaluated | 65 |
| Pyridine-Pyrazolone | 0.5 | Good | Orange | Fair | Fair | Reagents are unstable | Will not be evaluated | 45 |
| p-Nitrobenzenediazonium Chloride (Riegler's Reagent) | 0.7 | Sensitive to amines | Yellow-Red | Poor | Poor | Reagents are unstable | Will not be evaluated | 22 |
| Silver Nitrate & Formaldehyde | .05 | N.G. | Black or Silver | Fair | Fair | Photosensitive | Will not be evaluated | 12,20 |
| Silver Nitrate & Tannin | 0.1 | N.G. | Silver | Poor | Poor | Photosensitive | Will not be evaluated | 2,3,21 |
| Sodium Hypochlorite, Sulphanilamide, N-1 Napthyl-ethylenediamine Dihydrochloride | 20* | N.G. | Pink | Poor | Poor | Reagents are unstable | Will not be evaluated | 46 |
| Sodium Nitroprusside & Resorcinol | N.G. | Sensitive to volatile amines | Green or bluish green | Good | Good | | Will not be evaluated | 17 |
| Sodium Phenolate & Sodium Hypochlorite in presence of $MgCO_3$ | N.G. | N.G. | N.G. | Poor | Poor | | Will not be evaluated | 30 |
| Sodium Salicylate & Nitroprusside | 5 | Good | Blue | Good | Good | | Will be evaluated | 29,44 |
| Sodium Salicylate, Chlorine, and Sodium Hypochlorite | N.G. | N.G. | Blue | Poor | Poor | Reagents are unstable | Will not be evaluated | 33 |
| Thymol & Alkaline Bromine Water | 280 | N.G. | N.G. | Fair | Good | | Has been evaluated | 31, 54 |
| Thymol & Chloramine T | N.G. | N.G. | Blue | Fair | Fair | | Will be evaluated | 64 |
| Thymol in Ethyl Alcohol | 100 | N.G. | N.G. | Fair | Fair | Reagents are volatile | Will not be evaluated | 18 |

* ug in 1 liter of air
** mg in 1 liter of air
N.G. - Not given

subsequent qualification testing was carried out with these requirements in mind. They are listed in Table 3.

TABLE 3. ANALYTICAL REAGENT/REACTION REQUIREMENTS FOR EPA AMMONIA COLLECTOR/SENSORS

| | |
|---|---|
| 1. | Provide sufficient sensitivity to respond to the ranges of interest |
| 2. | Provide an analytical accuracy of about ±10% |
| 3. | Provide the required dynamic range |
| 4. | Provide the desired specificity under the conditions of use |
| 5. | Be compatible with the polymer solution matrix |
| 6. | Provide good optical properties in the final polymer reactant coating |
| 7. | Provide polymer reaction coating formulation which is not adversely affected by varying atmospheric conditions of relative humidity and temperature |
| 8. | Provide sufficiently fast response so that short-term, high concentration levels can be determined |
| 9. | Provide immediate reaction that does not require further analytical workup in the laboratory |
| 10. | Provide the required stability of the end products |

## 4.2 ANALYTICAL REACTION SCREENING

On the basis of the above mentioned analysis of potential reactions, screening of the most promising ones was carried out qualitatively on filter paper. The reagents were evaluated by observing the color change on filter paper when a small amount of reagent in solution was exposed to ammonium hydroxide in

deionized water. A blank was made by applying the reagent and deionized water only to filter paper. In addition, the compatibility of the screened reagents with polyvinyl alcohol polymer was determined. The results of the screening studies are shown in Table 4.

Tentatively, three reactions were selected for evaluation in coating form on quartz waveguides. These are:

1. Ferric Sulfate [$Fe_2(SO_4)_3$]
2. Ninhydrin (1,2,3-Triketohydrindene monohydrate)
3. Manganese Nitrate and Cuprous Chloride [$Mn(NO_3)_2$+ CuCl]

Upon exposure to ammonia the ferric sulfate is thought to chemically react to form ferric ammonium sulfate which has a violet color according to the equation shown below.[6]

$$2NH_{3(aq)} + 2Fe^{+3}_{(aq.)} + 4(SO_4)^{-2}_{(aq.)} + 2H^{+}_{(aq.)} \rightleftharpoons$$

$$Fe_2(SO_4)_3.(NH_4)_2SO_4$$

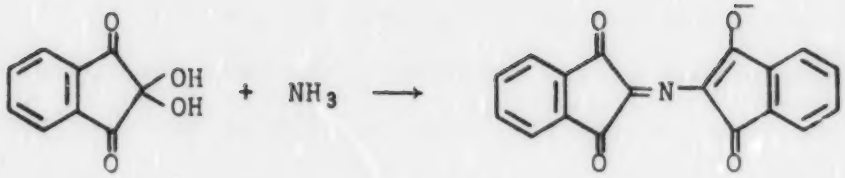
Ninhydrin (triketohydrindene hydrate) was considered as a possible reagent for the detection of low concentrations of ammonia based on the fact that an intense blue to reddish-violet color is formed above pH 2-3 when primary amino compounds are heated with ninhydrin and that this reagent supported on silica gel was used for the determination of $NH_3$ in air.[33] The intense color is due to the reaction of ninhydrin with the liberated ammonia to form the intensely colored compound shown

TABLE 4. LABORATORY EVALUATION OF AMMONIA REACTIONS

| Reagent/Reactant | Qualitative Spot Test Color Results[1] | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| | Reagent Concentration g/ml ($H_2O$) | Blank (Deionized Water) | Concentrated Ammonia Water | ~300 ppm $NH_3$ in Ammonia Water | Compatibility with PVA Polymer Matrix | Stability | | Remarks |
| | | | | | | Reagents | Reaction Products | |
| Ferric Sulfate | 0.1 | lt. brown | dk. brown | brown | good | good | good | sensitive reaction |
| Manganese Nitrate & Cuprous Chloride | 0.14 & 0.049 | colorless | dk. brown | brown | good | fair[3] | good | very sensitive reaction |
| Ninhydrin | 0.035 (saturated solution) | lt. blue | brown & blue | blue | good | good | good | very sensitive reaction |
| Cuprous Chloride & Tannin | 0.01 & 0.05 | lt. brown | yellow | brown | poor (brown precipitate) | good | good | incompatible with polymer matrix |
| Thymol & Alkaline Bromine Water | 0.1[2] & 0.018 | colorless | colorless | colorless | -- | -- | -- | No color reaction obtained |
| Phenol & Sodium Hypochlorite | 0.04 & 0.05 | colorless | colorless | colorless | good | good | good | color reaction observed only in solution |
| Alloxantine in Acetic Acid | <0.04 (saturated solution) | lt. brown | red | lt. red | good | good | good | sensitive reaction |
| Calcium Sulfate | <0.005 (saturated solution) | colorless | colorless | colorless | -- | -- | -- | no color reaction obtained |

[1]Spot tests were made on filter paper using equal volumes (~1 ml) of reagent and $NH_4OH$ in deionized water
[2]grams/ml (methanol)
[3]Precipitate forms after 24 hours

below.



The reaction is positive for ammonium salts and amines, and even very dilute solutions of ammonium salts will give a strong positive test. It was found that the reagent was especially sensitive to gaseous ammonia during chromatographic studies when paper chromatograms were sprayed with ninhydrin solution. Release of small quantities of ammonia into the room would color the entire chromatogram an intense blue to bluish-purple.

The manganese nitrate and cuprous chloride reagent is an attempt to replace the light sensitive silver nitrate by a copper I salt, in the reaction shown below.

$$MN^{+2} + 2\ Ag^{+} + 4OH^{-} \rightleftharpoons MnO_2 + 2A_g^{\circ} + 2H_2O$$

A brown precipitate forms when a Lewis base, such as $NH_3$, contributes an $OH^-$ ion in water.[16]

## 4.3 COATING

Using polyvinyl alcohol (PVA) polymer as a coating matrix,

2 cm x 0.1 cm diameter quartz rods (waveguides) were coated with polymer both with and without reagent. In early studies a rotating drum method was used which allows for the coating of between one and twelve rods at any one time. The rods were oriented so that as the drum rotated the rods, located on the pheriphery of the drum, entered the solution with their axis in a horizontal position. (See Figure 4). Upon each pass through the PVA solution the rods picked up a certain amount of polymer/reactant which was then dried by passing the rods under an infrared lamp. Drying was accomplished with the rods in position on the rotating drum holder to insure even distribution of the coating. The process conditions used in coating a number of waveguides and their properties are shown in Table 5. The use of a wetting agent was discontinued after observing no improvement in coating uniformity, especially with higher viscosity solutions. The best coatings were obtained by making one pass through the solution and air drying. Additional passes after drying caused the coating to wrinkle. This is probably due to the absorption of water from the second layer into the first layer.

The coating thickness was measured, using a micrometer caliper, at both ends and in the middle of each rod and an average is given in Table 5. In most cases, the coatings tended to be slightly oval in shape. The uniformity around the circumference of the rods appears to be good as determined using an optical

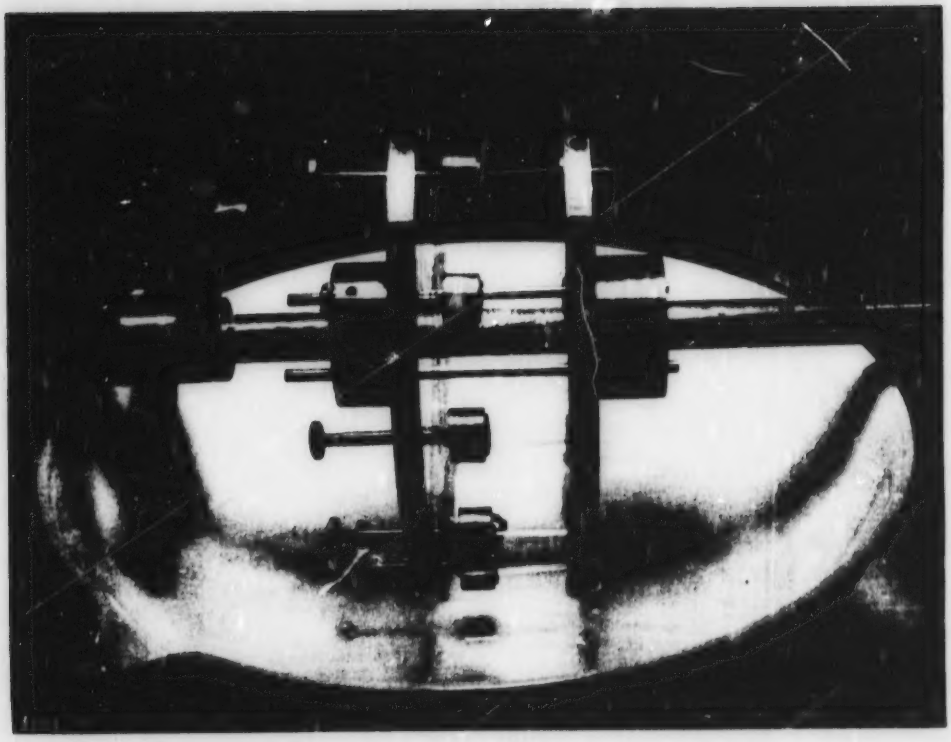


Figure 5. Rotating drum waveguide coating apparatus

TABLE 5. PROCESS CONDITIONS AND COATING PROPERTIES OF POLYMER/REAGENT COATINGS ON QUARTZ WAVEGUIDES (RODS)

| Set No. | # of Rods | Reagent | Coating Composition PVA, % wt. | Reagent % wt. | Average Coating Weight, g | Average Coating Thickness, microns | Color | Visual Appearance |
|---|---|---|---|---|---|---|---|---|
| 185334 | 4 | Ninhydrin | 93.5 | 6.5 | 0.0024 | 20 | Lt. Blue | Glossy transparent film |
| 185358 | 6 | Ninhydrin | 83.4 | 16.6 | 0.0014 | 25 | Lt. Blue | Glossy transparent film; faint color bands |
| 185399 | 6 | Ninhydrin | 83.4 | 16.6 | 0.0021 | 24 | Lt. Blue | Glossy transparent film; faint color bands |
| 185804 | 6 | Ninhydrin | 71.4 | 28.6 | 0.0031 | 36 | Lt. Blue | Glossy transparent film; faint color bands |
| 185343 | 6 | $Mn(NO_3)_2$ +CuCl | 89 | 9 | 0.0027 | 29 | Lt. Tan | Glossy transparent film; faint color bands; thicker on ends |
| 185360 | 6 | Alloxantin | 50 | 50 | 0.0015 | 18 | Lt. Pink | Glossy transparent film; faint color bands |
| 185361 | 4 | $Fe_2(SO_4)_3$ | 83.4 | 16.6 | 0.0030 | 28 | Lt.Brown | Glossy transparent film; thicker on ends |

All coatings made using 8.3 wt. % (PVA) polyvinyl alcohol in $H_2O$

Rods rotated at 1 RPM through solutions for 15 minutes and dried for 4 hours at 40°C

microscope.

A number of different reactants were incorporated into polymer solutions and applied to quartz waveguides. Coating solutions were also prepared using ninhydrin and a number of different polymers in order to determine any differences in coating characteristics. Summaries of these coating studies are given in Table 6 and Table 7. The variation in coating thickness and weight for different rods in the same set also shown in Table 6. The rods were coated in a similar manner with the exception that a different polymer was used with each set. Commercially available polymers were selected for this study on the basis of their transparency, solubility, and compatibility with ninhydrin. The uniformity from rod to rod in coating weight is considerably better than the thickness uniformity. Also the PVA polymer is considerably better than the other two polymers in coating weight uniformity.

In order to determine the reproducibility in transmission properties of 2 centimeter long collector/sensors, twenty-four rods were coated using the rotating drum method. Three sets of eight rods each were coated using optimized coating procedures. The coating thicknesses and weights were also determined and are tabulated in Table 7.

TABLE 6. VARIATION OF POLYMER/REAGENT COATING THICKNESS AND WEIGHT

| Polymer | PVA | HEC | PVP |
|---|---|---|---|
| Percent Polymer in Coating Solution | 8.3 | 14 | 24 |
| Reagent | Ninhydrin | Ninhydrin | Ninhydrin |
| Set No. | 185399 | 185393 | 185396 |
| # of Rods | 5 | 6 | 6 |
| Average Coating Weight,g | .0021 | .0015 | .0011 |
| Percent Weight Deviation | 14 | 26 | 21 |
| Average Thickness,microns | 24 | 37 | 20 |
| Percent Thickness Deviation | 26 | 19 | 46 |

PVA - polyvinyl alcohol, ICN Pharmaceuticals Inc. #2243 Lot 95848

HEC - hydroxyethyl cellulose, Cellosize, Union Carbide Corp., #QP-09L, Lot-W 1184-B

PVP - polyvinyl pyrrolidone, GAF Corp, Type NP-K30, Lot 40822

$$\text{Percent Deviation} = \frac{\text{Average Deviation}}{\text{Average (Weight or Thickness)}} \times 100$$ where

deviation is defined as the difference between the actual value and the average value of coating weight or thickness.

TABLE 7. COATING THICKNESS AND WEIGHT REPRODUCIBILITY OF PVA/ NINHYDRIN COATINGS MADE USING ROTATING DRUM METHOD

| Spec. No. | Coating Thickness, μ | Coating Weight, mg |
|---|---|---|
| 186818-1 | 55 | 1.8 |
| 186818-2 | 36 | 1.6 |
| 186818-3 | 36 | 2.7 |
| 186818-4 | 29 | 2.0 |
| 186818-5 | 38 | 2.1 |
| 186818-6 | 49 | 2.6 |
| 186818-7 | 36 | 1.7 |
| 186818-8 | 25 | 1.8 |
| 186819-1 | 38 | 2.5 |
| 186819-2 | 34 | 2.0 |
| 186819-3 | 52 | 2.6 |
| 186819-4 | 45 | 2.1 |
| 186819-5 | 51 | 2.3 |
| 186819-6 | 59 | 2.0 |
| 186819-7 | 51 | 2.0 |
| 186819-8 | 51 | 1.8 |
| 186820-1 | 41 | 3.0 |
| 186820-2 | 18 | 2.6 |
| 186820-3 | 42 | 2.4 |
| 186820-4 | 35 | 3.0 |
| 186820-5 | 38 | 2.4 |
| 186820-6 | 21 | 1.9 |
| 186820-7 | 34 | 2.3 |
| 186820-8 | 34 | 1.2 |

Average Thickness = 39μ

Standard Thickness Deviation (σ) = ±11μ

Average Weight = 2.2 mg

Standard Weight Deviation (σ) = ±.44 mg

Using the rotating drum coating method the concentration of polymer (polyvinyl alcohol) was varied in an effort to see the effect of coating solution viscosity on coating uniformity. However, no improvement in coating uniformity was obtained over that observed using the 8.3 wt.% PVA/ninhydrin solution found best in previous studies. Four centimeter long by 0.1 centimeter in diameter quartz rods were also coated following the same coating procedures used for 2 centimeter length rods. Coating nonuniformities were more prevalent with the longer rods. Apparently, the longer length minimizes end effects due to the rod holder and promotes the formation of bands as a result of surface tension forces. The 4 centimeter long rods were used in exposure studies to investigate the effect of collector/sensor length on transmission properties when exposed to ammonia.

In order to improve the coating uniformity a number of quartz rods both 2 and 4 centimeters in length were coated by holding at one end and slowly pulling out of the solution with the axis of the rod oriented vertically (vertical axis method). A rod holder was fabricated for this purpose which holds the rods at one end along the periphery of a cylindrical piece of aluminum as shown in Figure 5. The rods are placed into drilled holes and held by means of set screws. The holder is capable of holding forty rods for coating at one time. A Fischer-Payne dip coater is used at this time to pull the holder and rods in a vertical direction and at a

Figure 6. Rod holder for dip coating with beaker of polymer solution

uniform velocity out of a beaker containing the coating solution. These coatings tend to be much more uniform than coatings made using the rotating drum method. They are also thinner for a given viscosity solution. A slight variation in thickness from top to bottom was eliminated by rotating the rod 180° and coating a second time. This also allowed the coating to extend to the very end of the rod. The process conditions and coating properties of quartz rods coated using the vertical axis method are shown in Table 8. As would be expected those rods coated with the higher viscosity PVA solution were the thickest.

The rotating drum and vertical axis coating methods are compared in Table 9. The average thickness values given in Table 8 were measured using an optical comparator. Four diameter measurements were taken along the length of each rod. The total number of measurements for all the rods within a set was then averaged after subtracting out the diameter of the uncoated rod to determine the average thickness. In order to better define the deviation in thickness along the length of a rod, the maximum thickness reading for each rod within a set was then selected and an average maximum thickness determined for the set. The same was done for the minimum thickness readings to determine the average minimum thickness. As can be seen in Table 8 the percent deviation is considerably higher for those rods coated using the rotating drum method. The difference is larger in the case of the 4 centimeter length rods. Also, the

TABLE 8. PROCESS CONDITIONS AND COATING PROPERTIES FOR RODS COATED USING VERTICAL AXIS METHOD

| Specimen Number | Rod Length, cm | Coating Solution Wt %, PVA | Coating Composition PVA Wt % | Coating Composition Ninhydrin, Wt % | No. of Coats | Coating Thickness, μ | Visual Appearance | Remarks |
|---|---|---|---|---|---|---|---|---|
| 185244-1 | 4 | ~5 | 70 | 30 | 1 | <5 | smooth and uniform | Coating very thin |
| 185244-2 | 4 | ~5 | 70 | 30 | 2 | ~5 | smooth and uniform | specimen reversed for second coat |
| 185241-1 | 4 | ~10 | 70 | 30 | 1 | 15 | smooth and uniform | |
| 185241-4 | 4 | ~10 | 70 | 30 | 1 | 10 | smooth and uniform | |
| 185233-1 | 2 | ~15 | 80 | 20 | 2 | 38 | smooth; slightly thicker in center | specimen reversed for second coat |
| 185233-4 | 2 | ~15 | 80 | 20 | 1 | 10 | smooth and uniform | |

All specimens pulled with the rod axis in a vertical position at 5.2 cm/min from the coating solution and air dried for ~2 hours before recoating or placing in sealed containers.

TABLE 9. COMPARISON OF COATING METHODS

| Set No. | No. of Specimens | Coating Method | Rod Length | Average[1] Thickness | Maximum Thickness Readings | | Minimum Thickness Readings | |
|---|---|---|---|---|---|---|---|---|
| | | | | | Average Maximum Thickness | Percent Deviation[2] | Average Minimum Thickness | Percent Deviation[2] |
| 185233 | 6 | Vertical Axis | 2 cm | 15 μ | 23 μ | 50 | 8 μ | 50 |
| 186818 | 6 | Rotating Drum | 2 cm | 41 μ | 58 μ | 87 | 10 μ | 75 |
| 185241 | 4 | Vertical Axis | 4 cm | 13 μ | 18 μ | 40 | 5 μ | 60 |
| 186821 | 5 | Rotating Drum | 4 cm | 69 μ | 125 μ | 81 | 13 μ | 81 |

[1]Average Thickness determined by measuring at small intervals along the length of each rod within a set.

[2]Percent deviation = $\Sigma \frac{\text{Max. or Min. Avg. Thickness - Avg. Thickness}}{\text{Avg. Thickness}} \times 100$

average thickness is less in the case of those coatings made using the vertical axis method even though the same coating solution (8.3 wt.% PVA/ninhydrin) was used.

In the vertical axis coating method, the entire length of the rod is coated, the rod is reversed and a second coat is applied. The coating on the flat end is then easily removed with a sharp knife or razor blade. A higher viscosity solution (~ 15 wt.% PVA) than used with the rotating drum coating method was found necessary to achieve a comparable coating thickness. A numerical bubble viscosimeter was used to achieve reproducible coating solutions.

Table 10 shows the degree of reproducibility obtained in both coating weight and thickness for rods coated with PVA/ninhydrin using the vertical axis method. In general, the results show an improvement in coating reproducibility be a factor of five. Consequently, this technique was used for all further work throughout this program.

Additional coating studies were carried out using quartz which were dip coated using the vertical axis method from solutions containing either polyvinyl alcohol (PVA) and/or polyvinyl pyrrolidene (PVP polymer and ninhydrin reagent. In several experiments glycerin was added to the PVA solution to improve the hygroscopic properties of the coating. Since the PVP has better

TABLE 10. COATING THICKNESS AND WEIGHT REPRODUCIBILITY OF PVA/NINHYDRIN COATINGS MADE USING VERTICAL AXIS METHOD

| Spec. No. | Coating Thickness, μ | Coating Weight, mg |
|---|---|---|
| 186885-1 | 20.3 | 3.0 |
| 186885-2 | 30.5 | 2.3 |
| 186885-3 | 33.0 | 2.6 |
| 186885-4 | 30.5 | 3.0 |
| 186885-5 | 27.9 | 2.2 |
| 186885-6 | 30.5 | 2.5 |
| 186885-7 | 33.0 | 1.6 |
| 186894-1 | 27.9 | 1.9 |
| 186894-2 | 25.4 | 1.9 |
| 186894-3 | 30.5 | 1.6 |
| 186894-4 | 33.0 | 1.8 |
| 186894-5 | 25.4 | 2.2 |
| 186894-6 | 20.3 | 1.8 |
| 186897-1 | 30.5 | 3.6 |
| 186897-2 | 33.0 | 2.2 |
| 186897-3 | 25.4 | 2.4 |
| 186897-4 | 27.9 | 2.5 |
| 186897-5 | 25.4 | 2.5 |
| 186897-6 | 40.6 | 2.6 |
| 186897-7 | 33.0 | 2.4 |

| | |
|---|---|
| Average Thickness | = 29.2μ |
| Standard Thickness Deviation (σ) | = ± 4.8 |
| Percent Thickness Deviation | = ±16.4 |
| Average Weight | = 2.33mg |
| Standard Weight Deviation (σ) | = ± 0.503 |
| Percent Weight Deviation | = ±21.6 |

hygroscopic properties than the PVA and it should allow better sensitivity to ammonia in dry air conditions. Table 11 shows the coating properties for quartz rods coated using various coating solutions. The variation in properties are due, in most cases, to viscosity differences in the solutions. The solution characteristics can be modified by varying the polymer molecular weight with no adverse effect on polymer hygroscopicity.

## 4.4 EXPOSURE TO AMMONIA OF POLYMER/REAGENT COATINGS ON WAVEGUIDES

Individual coated quartz rods containing the reagents shown in Figure 7 were placed in a desiccator containing ammonia water. Sister samples were placed in another desiccator containing only distilled water. The color change observed in the ammonia exposed rods was quantitatively determined by measuring the light transmission axially down the waveguide as a function of time. The results are shown in Figure 7. The ninhydrin reagent samples showed the largest drop in transmission although all but the alloxantin had acceptable changes in transmission.

In order to determine the characteristics of the collector/sensors at lower levels of ammonia concentration a precision gas calibration system was purchased capable of achieving parts/billion $NH_3$ concentrations in a dilute gas stream. The system uses sealed permeation tubes which contain liquid ammonia for the 0.5-500 ppm levels. For lower levels an ultra low emission

TABLE 11. PROCESS CONDITIONS AND COATING PROPERTIES FOR RODS COATED WITH A NUMBER OF DIFFERENT POLYMERS AND POLYMER COMBINATIONS USING VERTICAL AXIS METHOD

| Set # | Rod Length cm | Polymer** | Coating Solution wt.% | Coating Composition | | # of Coats | Coating Thickness μ | Visual Appearance | Remarks |
|---|---|---|---|---|---|---|---|---|---|
| | | | | Polymer wt.% | Ninhydrin wt.% | | | | |
| 189507 | 2 | *PVA/ glycerin | 11 | 79 | 21 | 2 | 19.2 | smooth & uniform | Specimen reversed for second coat |
| 189514 | 2 | PVA | 11 | 79 | 21 | 2 | 19.3 | smooth & uniform | Specimen reversed for second coat |
| 189518 | 2 | PVA | 11 | 79 | 21 | 2 | 11.9 | smooth & uniform | Specimen reversed for second coat |
| 189525 | 2 | *PVA/ glycerin | 11 | 79 | 21 | 2 | 17.2 | smooth & uniform | Specimen reversed for second coat |
| 189527 | 2 | *PVA/ glycerin | 11 | 79 | 21 | 2 | 24.9 | smooth; slightly thicker on ends | Specimen reversed for second coat |
| 189537 | 2 | PVA | 11 | 79 | 21 | 2 | 13.4 | smooth & uniform | Specimen reversed for second coat |
| 189539 | 2 | PVA | 11 | 79 | 21 | 2 | 15.1 | smooth & uniform | Specimen reversed for second coat |
| 189542 | 2 | PVA | 11 | 79 | 21 | 2 | 14.9 | smooth & uniform | Specimen reversed for second coat |
| 189511 | 2 | PVP K-90 | 9 | 75 | 25 | 2 | 5.9 | smooth & uniform | Specimen reversed for second coat |
| 189535 | 2 | PVP K-90 | 9 | 75 | 25 | 2 | 6.8 | smooth & uniform | Specimen reversed for second coat |

* 1μl glycerin was added per 100 ml coated solution.
All specimens pulled with the rod axis in a vertical position at 5.2 cm/min from the coating solution and air dried ~2 hrs. before recoating.
**PVA (Lot #95848) obtained from ICN Pharmaceuticals Inc.; PVP (Type NP-K-90) obtained from GAF Corporation

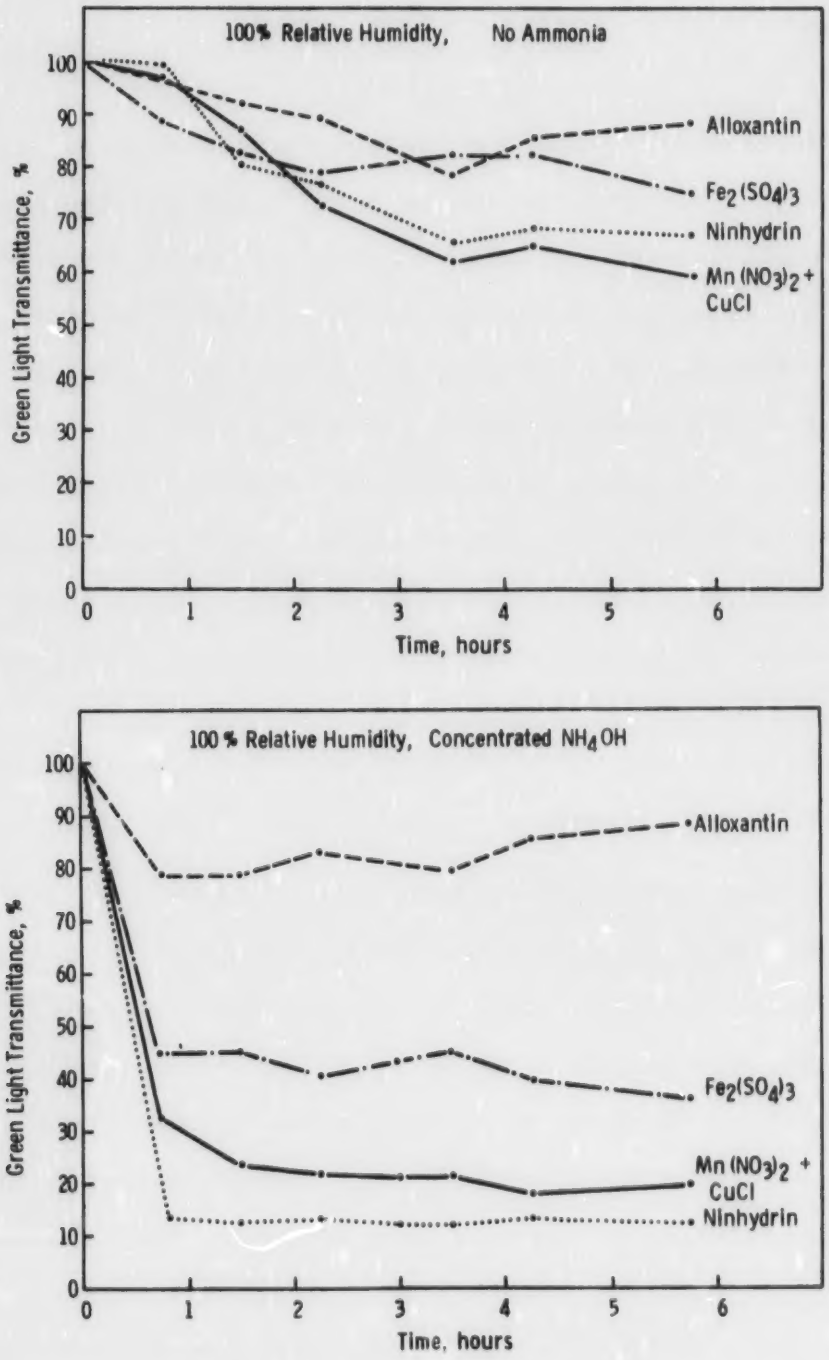



Figure 7. The effect of high humidity and/or concentrated $NH_4OH$ on the transmission properties of PVA/reagent coated rods

membrane housed in a stainless steel cartridge is used. It is capable of achieving low parts/billion levels of $NH_3$ in a diluent gas stream.

Several PVA/ninhydrin coated collector/sensors were exposed to ∿1 ppm $NH_3$ in a diluent air stream of ∿375cc/min. The change in light transmission was determined after 1.5 hours and 2 hours as shown in Figure 8. Using dry air essentially no reaction occurred. However, using nearly saturated air a colorimetric reaction occurred along with an appreciable reduction in transmission due to the presence of ammonia, whereas, blank runs evidenced little change in transmission. Additional experiments were conducted to better determine the relationship between relative humidity and reaction time.

## 4.5 EXPOSURE TO AMMONIA OF POLYMER/REAGENT COATINGS ON QUARTZ WAVEGUIDES TO DETERMINE EFFECT OF GAS STREAM VELOCITY

Experiments were conducted to determine the effect of gas velocity over the surface of the coated quartz rods on transmittance during exposure studies. To accomplish this a modified experimental arrangement as shown in Figure 9b was required. The first configuration shown in Figure 9a uses a glass tube specimen chamber. This experimental configuration was used for most of the exposure studies up to this time. The calculated gas velocities obtained with a 0.178 $cm^2$ cross sectional area glass tube were ∿2200 cm/min. By splitting the gas flow and

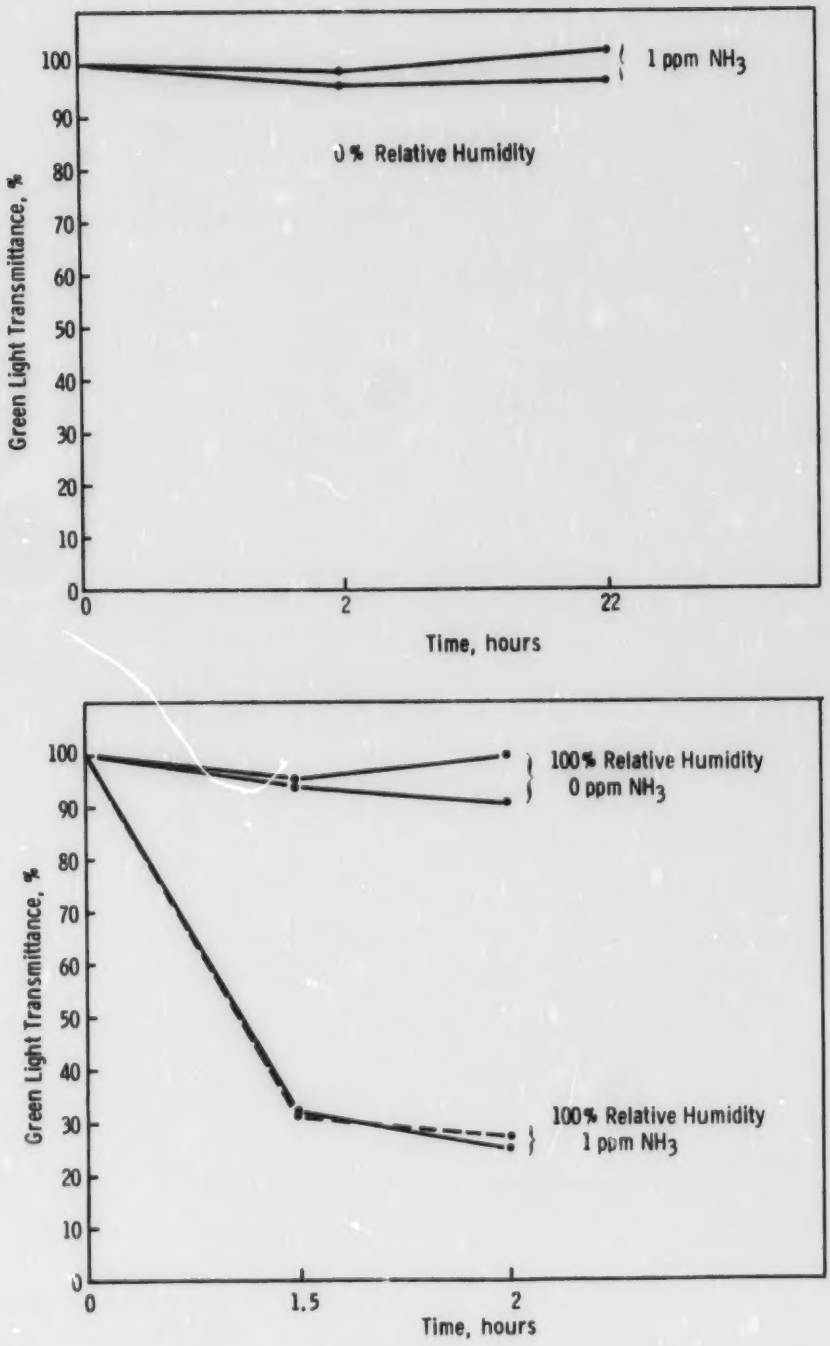
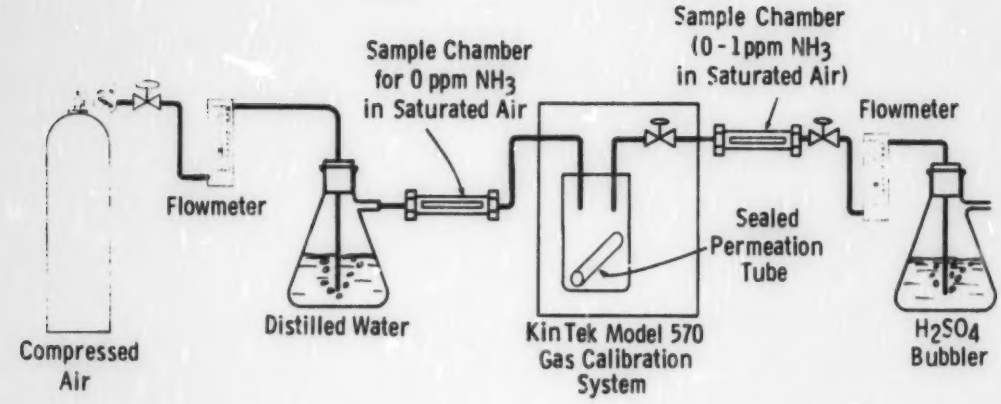
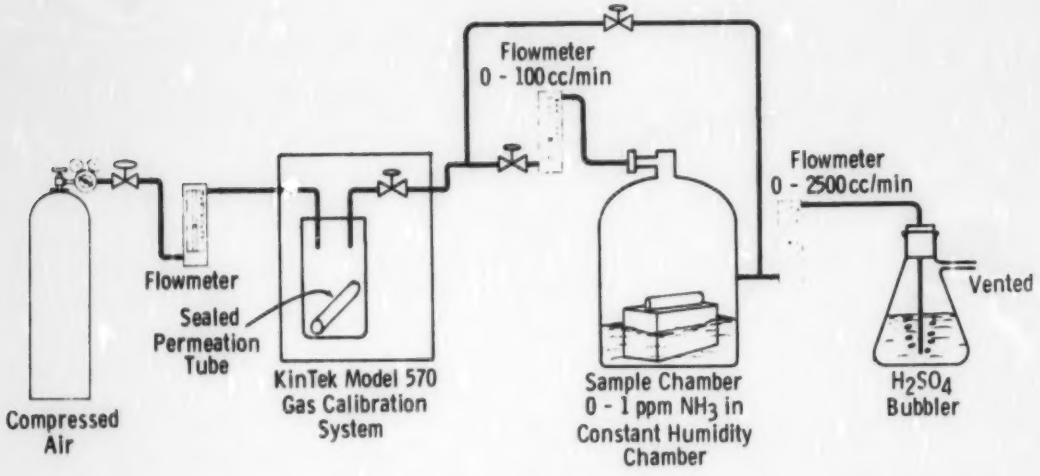



Figure 8. The effect of both low and high humidity on PVA/ninhydrin coated rods exposed to 0 & 1 ppm ammonia concentrations in an air stream.




a. High velocity air stream




b. Low velocity air stream

Figure 9. Schematic of equipment used to expose collector/sensors to known concentrations of ammonia in air.

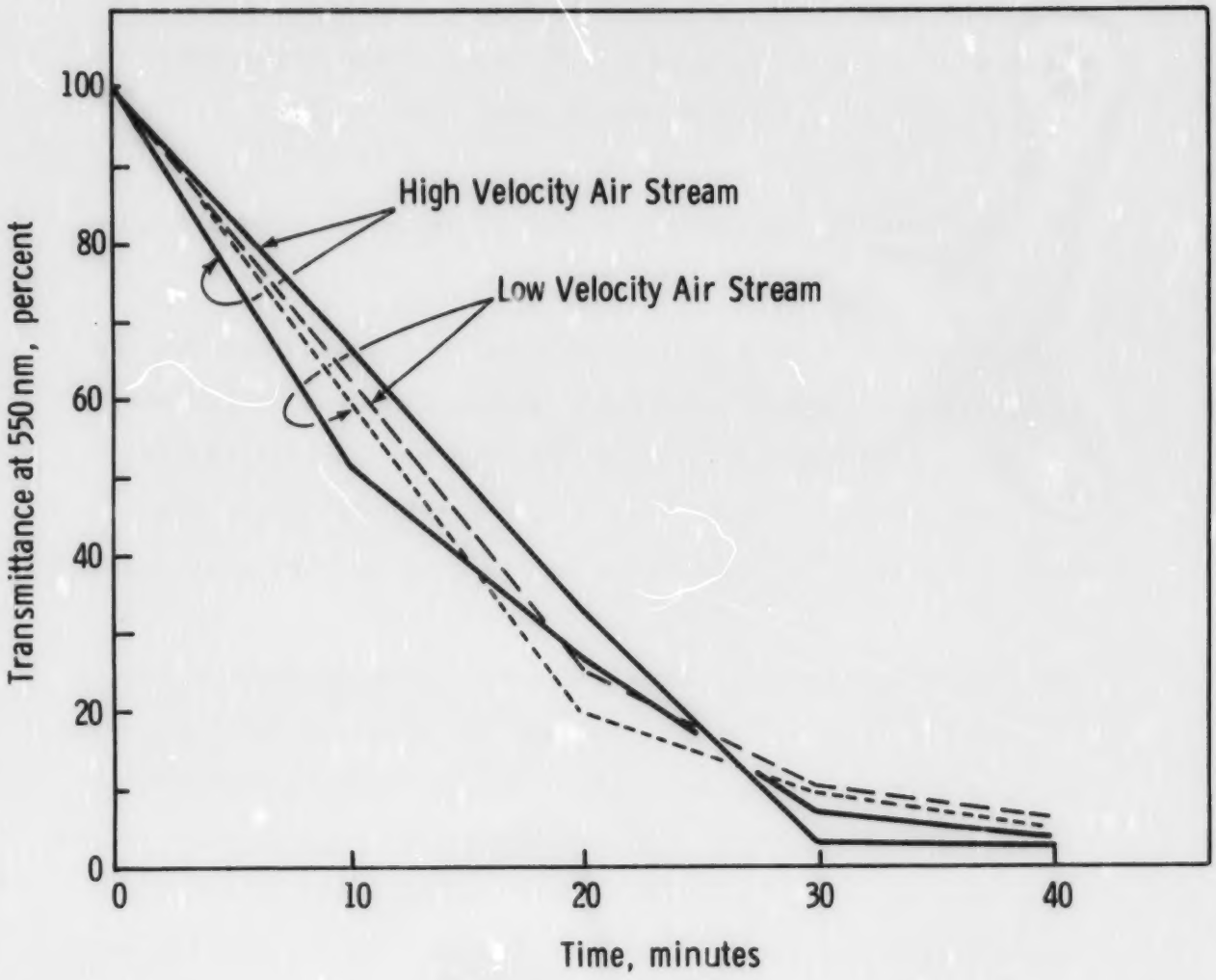



Figure 10. Transmittance of 2 cm long collector/sensors as a function of exposure time and air stream velocity.

using a larger diameter desiccator chamber, as shown in Figure 9b. Essentially no difference was observed in collector/sensor transmittance as a function of time for specimens exposed to the same ammonia concentration using two different gas stream velocities as shown in Figure 10. In field sampling the collector/sensors would never be used where the gas velocities would be less than these specimens were exposed to.

## 4.6 SENSITIVITY AND DYNAMIC RANGE OF COLLECTOR/SENSOR AND EFFECT OF RELATIVE HUMIDITY

Earlier work had shown that little or no reaction between the ninhydrin and ammonia took place at low humidity conditions. By mixing known amounts of dry air with the humidified air, different relative humidities were created which were used to test the effect of humidity on various reactant polymer coatings.

The curves in Figure 11 show the comparative hygroscopicity of various polymers. Both the PVP and PVA polymers have been used to form coatings on quartz rods. As the relative humidity decreases one would expect the PVP (polyvinyl pyrrolidene) to retain more moisture than the PVA and consequently remove more ammonia from the surrounding air when used in conjunction with ninhydrin as a coating matrix. Therefore, the relationship between relative humidity and collector/sensor transmittance should follow the general shape of the curves shown in Figure 12. The PVA would exhibit better handling characteristics at the

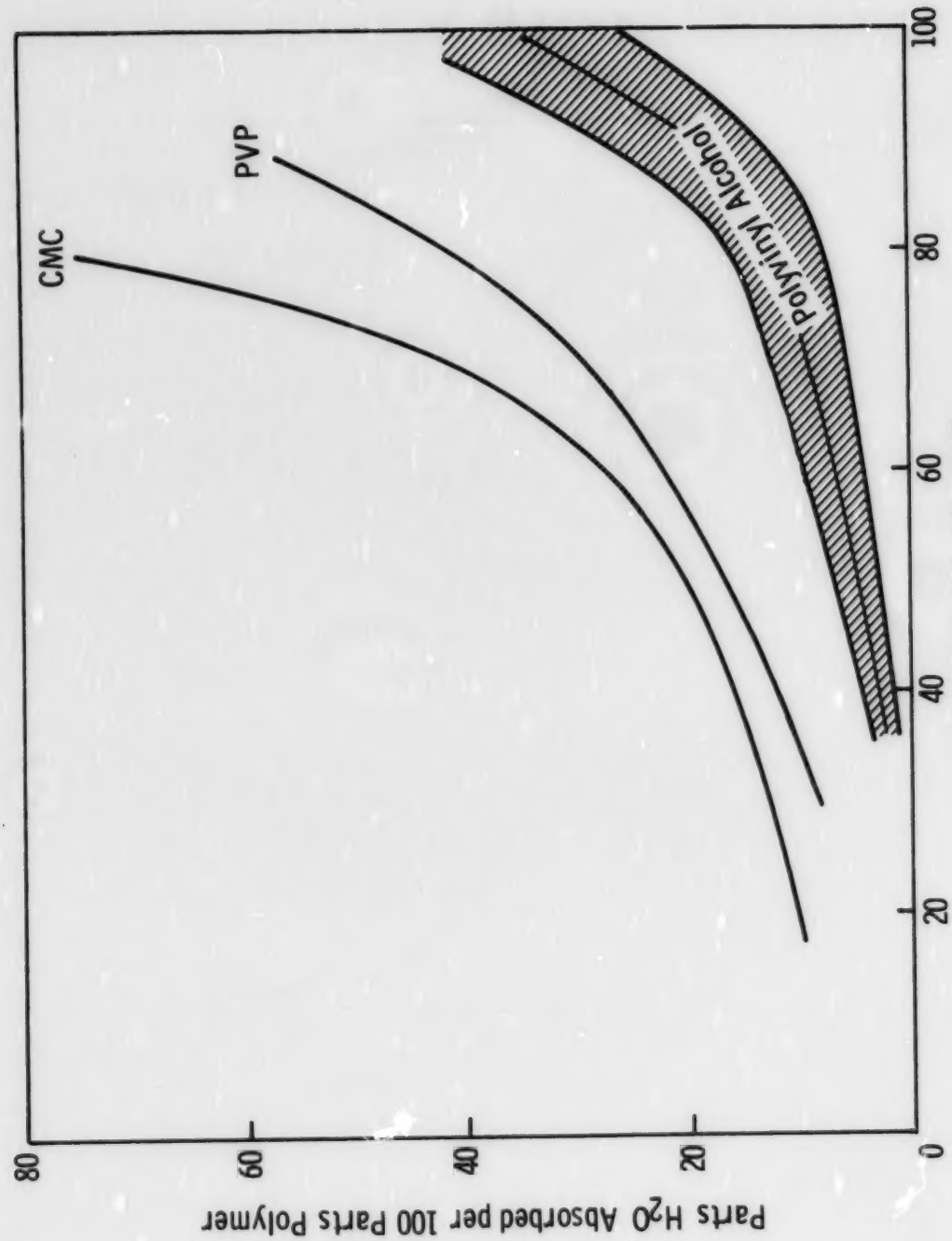



Figure 11. Hygroscopity of various polymers (Ref. 3)

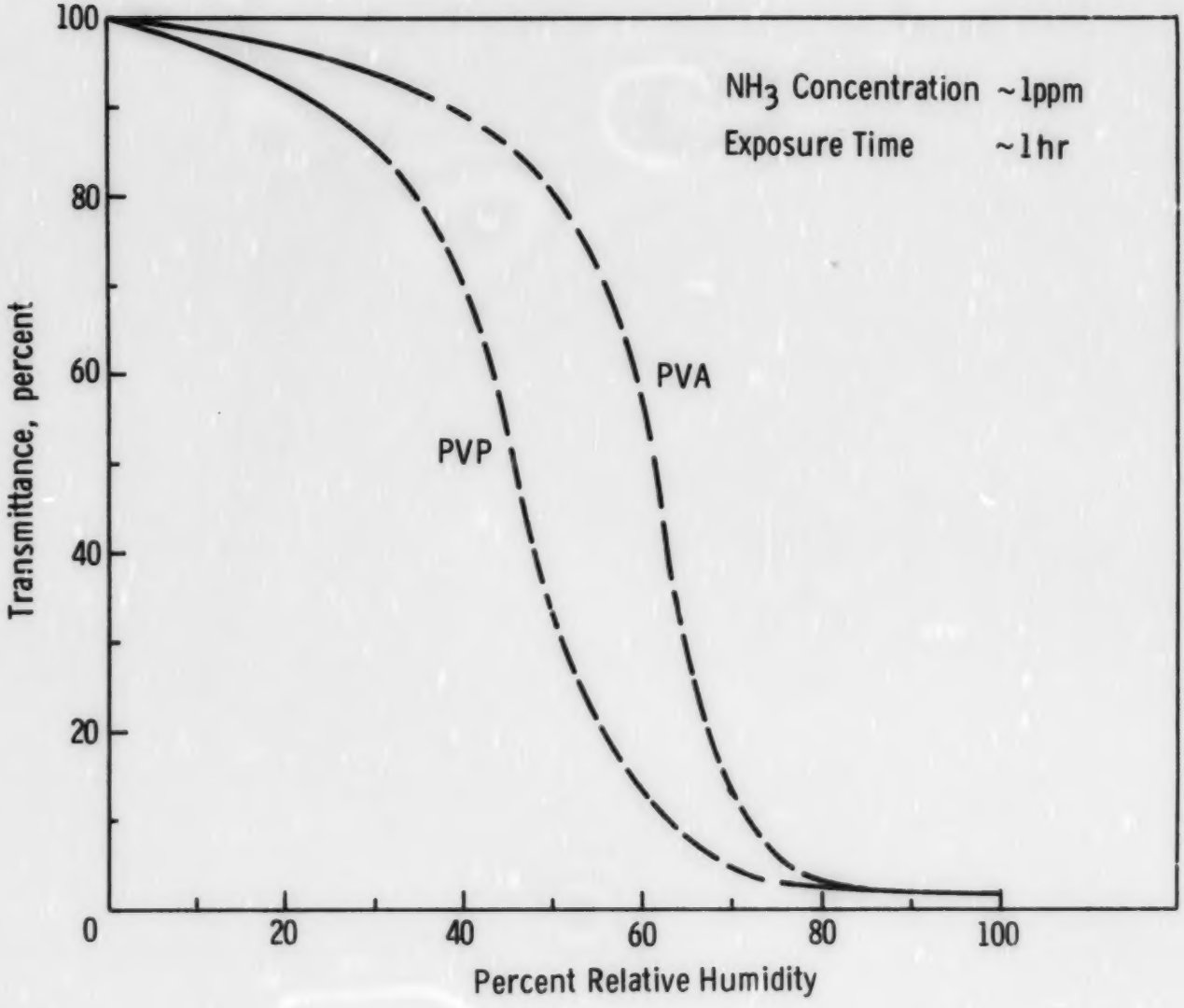



Figure 12. Effects of relative humidity on collector/sensor sensitivity to ammonia.

higher humdities because of the lower solubility in water of this polymer. However, at the lower humidities the PVP should provide better sensitivity to ammonia.

Earlier exposure studies were made at a fixed ammonia concentration of 1 ppm and usually at high humidity levels. To investigate other $NH_3$ concentrations the low emission membrane was incorporated into the Kin Tek Model 570 gas calibration system. Using the membrane, concentrations as low as 15 ppb ammonia can be achieved in a moving air system. Figure 13 shows a schematic of the experimental apparatus used in exposure studies. Different relative humidities were obtained in the diluent air stream by adjusting the flow rate through the distilled water bubbler.

### 4.6.1 Effect on Sensitivity of Coating Polymer Type

PVA, PVA-Glycerin and PVP polymers were investigated in rod coating studies as matrix materials for the ninhydrin reagent. Coated quartz rods (collector/sensors) had different sensitivities to low concentrations of ammonia depending on the polymer system. In general, the PVP/ninhydrin coating provided the best sensitivity as shown for a particular concentration and relative humidity in Figure 14. The least sensitive coating system was the PVA-Glycerin. Therefore, further work emphasized PVP/ninhydrin coatings.

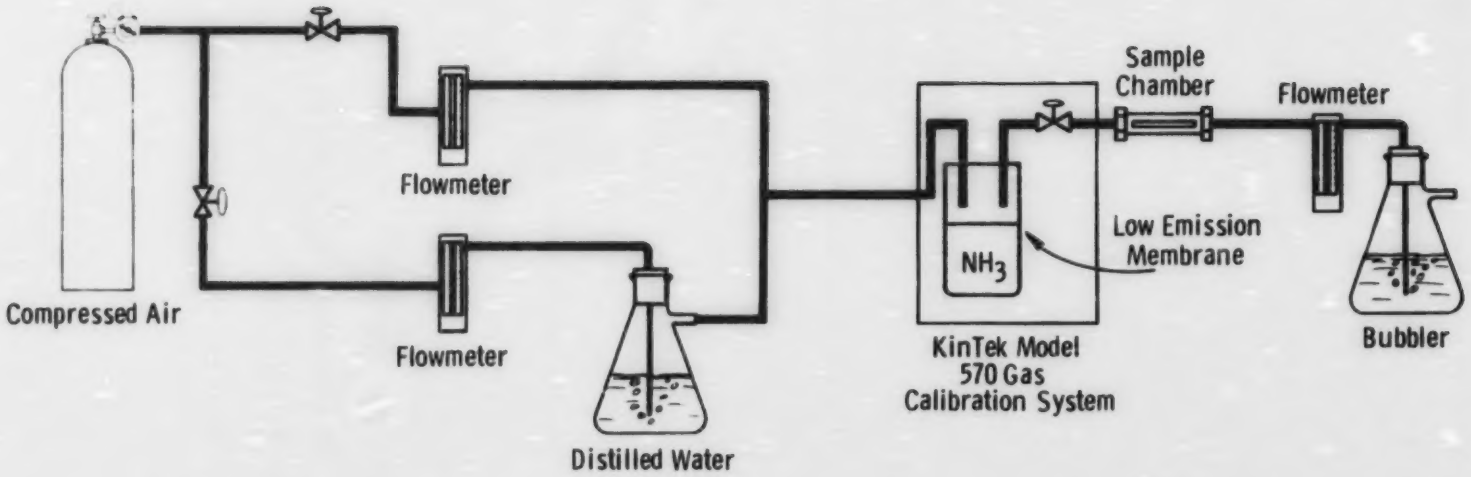



Figure 13. Schematic of equipment used to expose collector/sensors to known concentrations of ammonia in air.

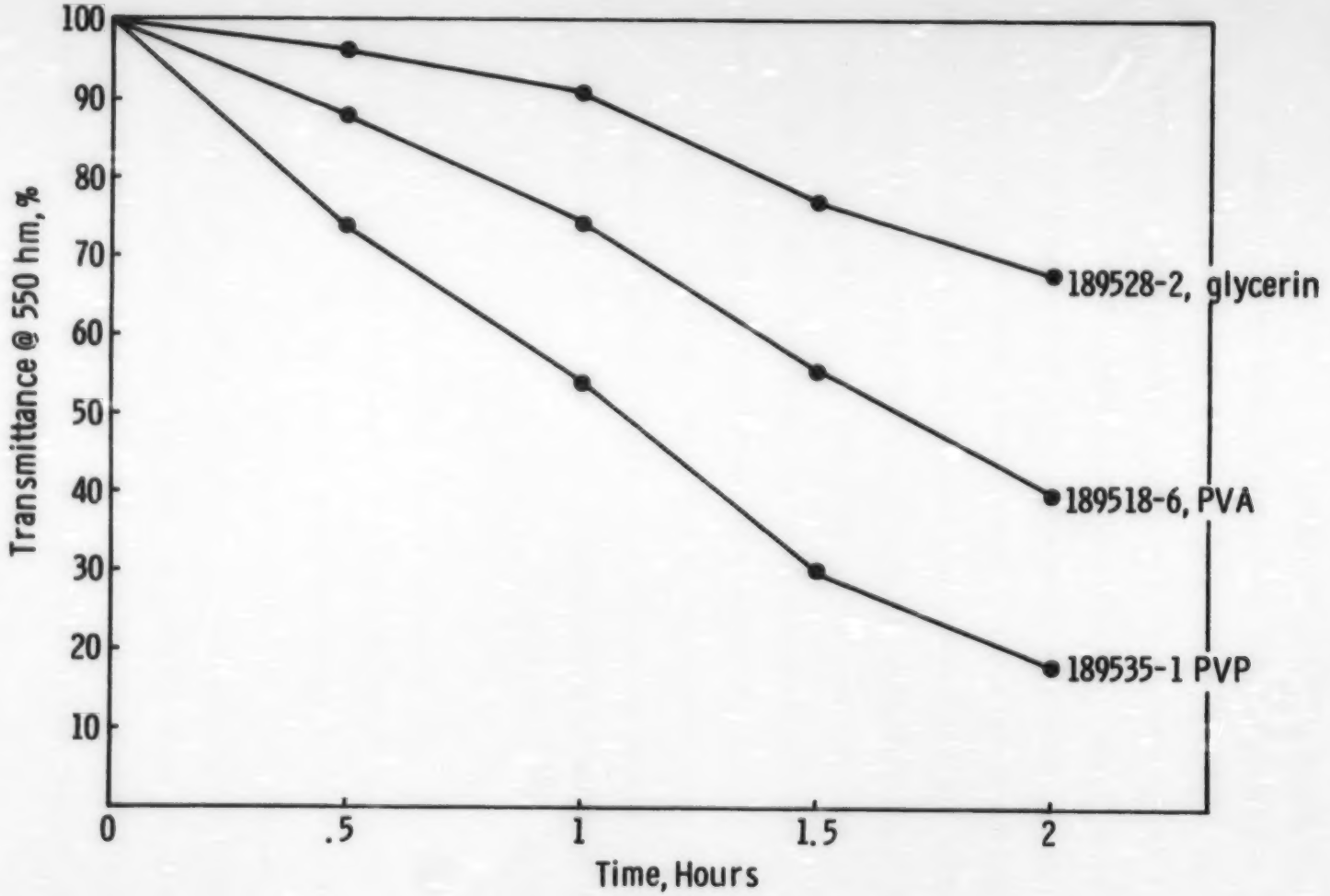



Figure 14. The effect of polymer coating type on collector/ sensor response using ninhydrin reagent

### 4.6.2 Effect of Ammonia Concentration on Collector/Sensor Response

Initial collector/sensor calibration studies were made at relatively high humidity levels (∿80 R. H.) where maximum sensitivity to ammonia is observed. Three ammonia concentrations below 1 ppm were selected for study. Exponential transmission decay curves were obtained for each concentration as a function of exposure time. Essentially straight lines were obtained for the log transmission vs. exposure time with the slope of each line dependent on the concentration of $NH_3$ in air. Figure 15 and 16 show the percent change in transmission of PVP/ninhydrin and PVA/ninhydrin coated collector sensors, respectively, as a function of ammonia concentration and exposure time. From these experiments, it appears that at high humidity levels both the PVA and PVP polymers retain sufficient moisture to collect ammonia from the ambient air and allow measurement of the ammonia concentration.

Sensitivity is uniformly lower for both polymers at low humidities. This is shown in Figure 17 for concentration of 600 ppb ammonia in air at three humidity levels using PVP/ninhydrin collector/sensors. As can be seen the sensitivity is greatly enhanced at high humidities. Even so, a measurable response is obtained at the 45% relative humidity level with PVP/ninhydrin coatings. Figure 18 shows the response as a function of ammonia concentration and exposure time for two humidity levels

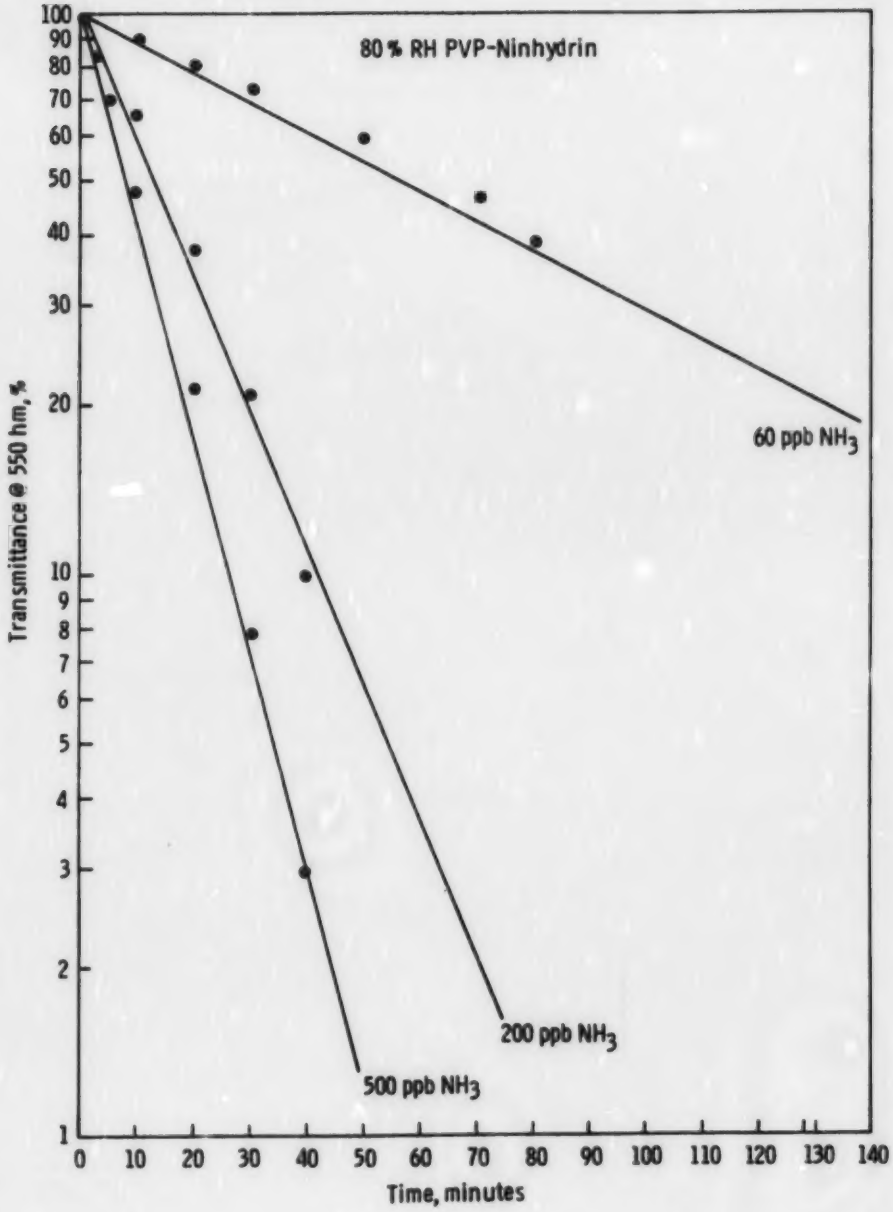



Figure 15. The sensitivity of PVP/ninhydrin collector/sensors at different ammonia concentration in air

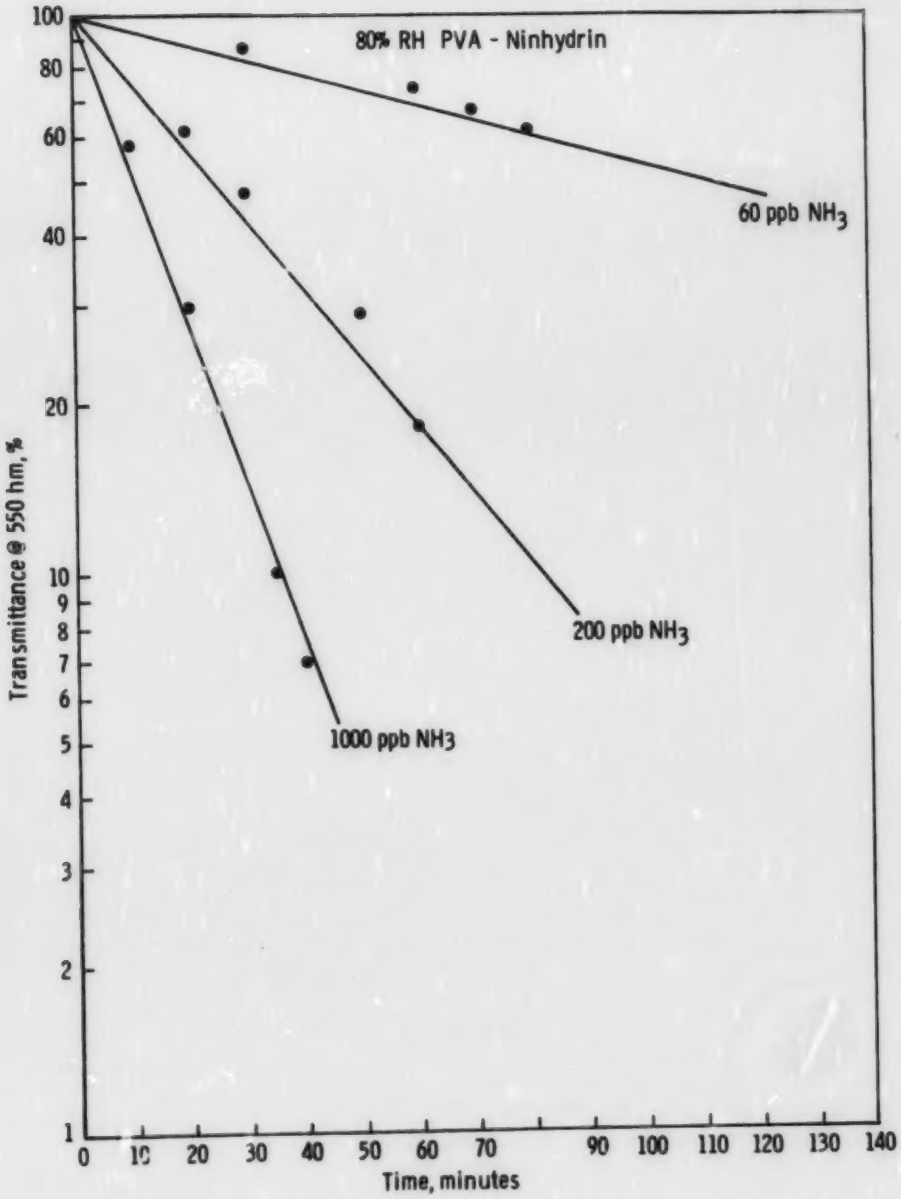



Figure 16. The sensitivity of PVA/ninhydrin collector/ sensors at different ammonia concentration in air

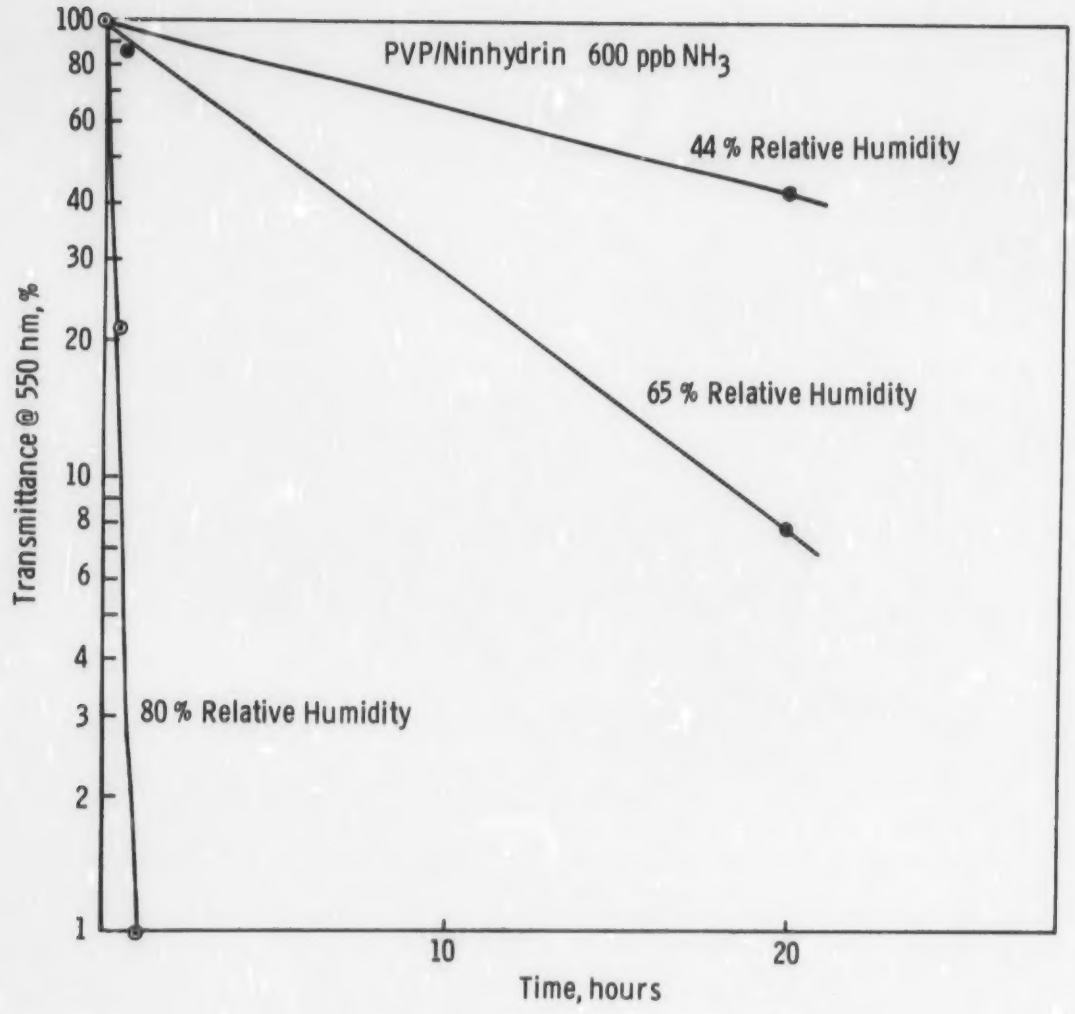



Figure 17. The effect of relative humidity on collector/sensor response at a fixed concentration of ammonia in air.

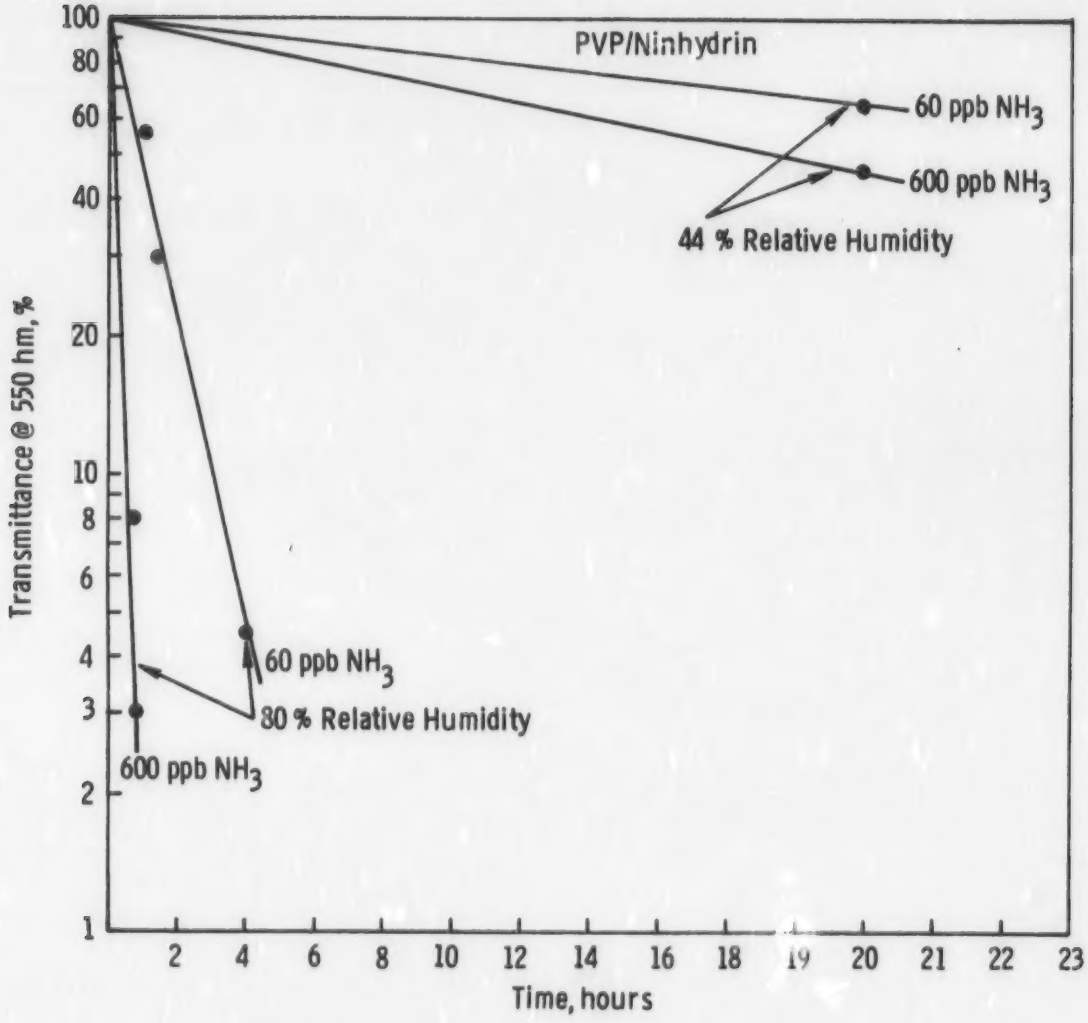



Figure 18. The effect of relative humidity on PVP/ ninhydrin collector/sensor response at two ammonia concentrations in air

using PVP/ninhydrin coated collector sensors. A measurable difference in response even at low relative humidity was obtained. By contrast, using PVA/ninhydrin coatings poor response as a function of ammonia concentration at 45% relative humidity. The lower hygroscopicity of the PVA polymer results in an excessive loss of moisture from the coating which in turn impedes the ammonia ninhydrin reaction.

By plotting the slope of the log transmission vs. time curves shown in Figure 15, at each known concentration, one can determine any unknown concentration. A plot of slope vs. concentration using PVP/ninhydrin coated collector/sensors is shown for a humidity of ∿80% in Figure 19.

## 4.7 STABILITY OF COLLECTOR/SENSORS

Stability studies were made in which both PVP (polyvinyl pyrollidone and PVA (polyvinyl alcohol)/ninhydrin coated quartz rods were stored in a dark area at constant humidity (60%) and temperature (25°C). The results of these studies after a one-week period are shown in Table 12. The changes in transmittance values are negligibly small compared to the changes encounted after exposure to even low concentrations of ammonia and are nearly within the experimental error of the GLAD instrument.

In addition the long term stability studies with PVA/ninhydrin coated quartz rods was continued and the results are shown in

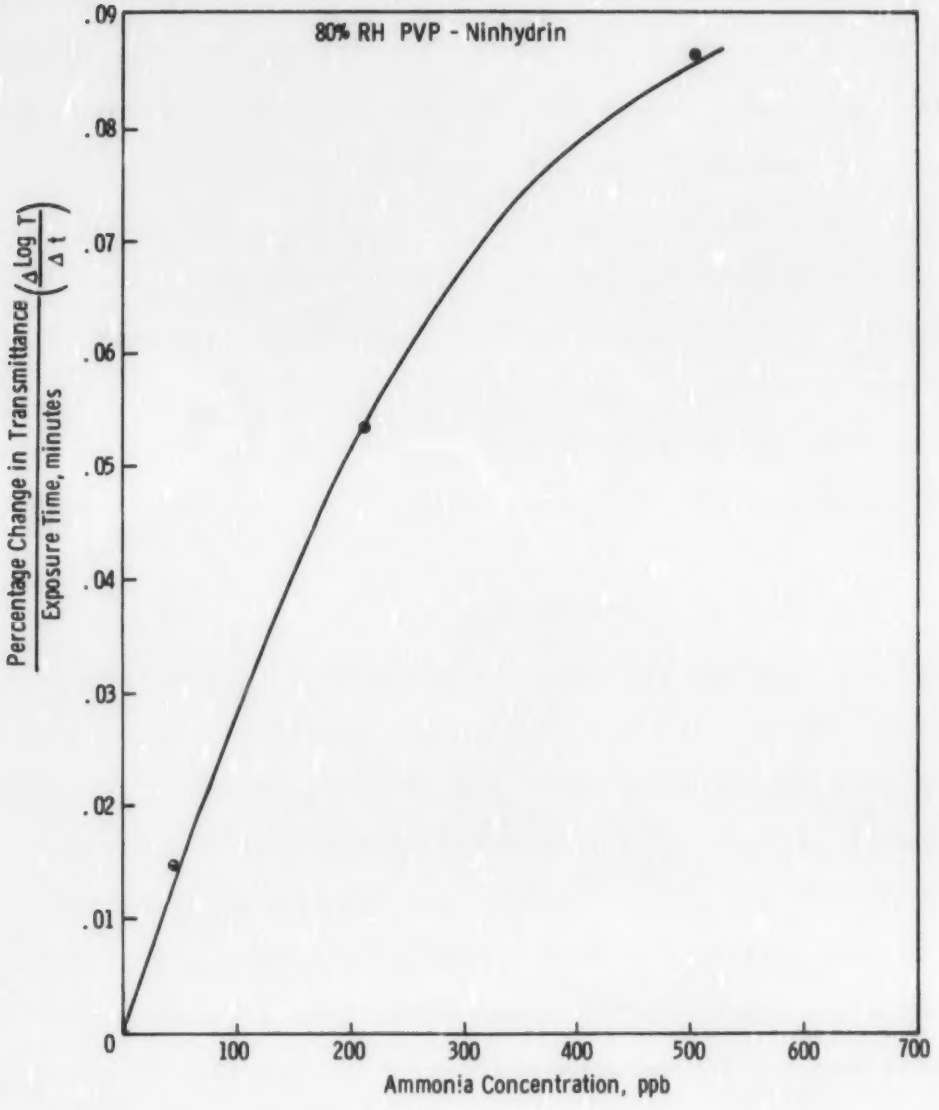



Figure 19. The slope of PVP/ninhydrin collector/sensor transmittance curves as a function of ammonia concentration in air

**TABLE 12. STABILITY OF POLYMER/NINHYDRIN COATED COLLECTOR/SENSORS**

| Spec. No. | Polymer | Specimen History | Elapsed Time, hr. | Transmittance Readings* Initial | | Final | | Percent Change in Transmittance | |
|---|---|---|---|---|---|---|---|---|---|
| | | | | White | 550nm | White | 550nm | White | 550nm |
| 190101-4 | PVP | Unexposed | 192 | 239.5 | 28.7 | 232 | 27.3 | -3 | -4.9 |
| 190101-5 | PVP | Unexposed | 192 | 224.5 | 26.8 | 211.5 | 24.8 | -5.8 | -7.3 |
| 190103-4 | PVA | Unexposed | 192 | 281 | 33.6 | 269 | 31.8 | -4.2 | -5.5 |
| 190103-5 | PVA | Unexposed | 192 | 333.5 | 39.5 | 319.5 | 38 | -4.2 | -3.8 |

* Measurements were made using GLAD II

Table 13. In all cases, the unexposed specimens showed the largest drop in transmission as would be expected. A high degree of consistency is shown from sample to sample for the total change in transmission. This may make it possible to predict the rate of light transmission change for a given time between actual collector/sensor manufacture and exposure. If this does not prove feasible the transmittance of collector/sensors would necessarily be measured in the field before and after exposure.

An alternate approach of evaluating changes during storage is to isolate the transmission changes not specifically associated with the ammonia reaction. This approach, as discussed previously, indicates that even on the unexposed C/S a 5% - 7% change is all that is obtained.

An additional set of PVA/ninhydrin coated collector/sensors, stored in a laboratory with minimal humidity or temperature control, were also remeasured after ~100 days as shown in Table 14. The $\Delta\%T/\Delta t$ of these specimens appeared to decrease sharply since the previous measurement approximately one month ago. Therefore, the transmittance values of PVA/ninhydrin coated collector/sensors after ~one month of the time of manufacture appear to stabilize and decrease at a much slower rate. These results have been substantiated during the remainder of the program including the field testing phases.

TABLE 13. LONG TERM STABILITY OF PVA/NINHYDRIN COATED COLLECTOR SENSORS

| Spec. No. | History | Elapsed Time(t)days | Transmittance Readings Initial White | Initial 700nm | Initial 550nm | Final White | Final 700nm | Final 550nm | Percent Change in Transmittance (Δ%T) White | Δ% 700nm | Δ% 550nm | Average Rate of Percent Change in Transmittance $\frac{\Delta\%T}{\Delta t}$, $\frac{\%}{days}$ White | 700nm | 500nm |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | 39 | 184 | 13.9 | 18.9 | 184 | 12.6 | 17.5 | 0 | - 9.3 | - 7.4 | 0 | -0.233 | -0.190 |
| | | 71 | 184 | 13.9 | 18.9 | 155 | 9.8 | 15 | -15.7 | -29.5 | -20.6 | -0.221 | -0.415 | -0.349 |
| 186885-3 | Unexposed | 102 | 184 | 13.9 | 18.9 | 153 | 10 | 14.2 | -16.7 | -28 | -24.8 | -0.164 | -0.275 | -0.243 |
| | | 39 | 234 | 15.4 | 25.4 | 232 | 15 | 23.6 | - 0.74 | - 2.6 | - 7.1 | -0.019 | -0.067 | -0.183 |
| | | 71 | 234 | 15.4 | 25.4 | 194 | 12.1 | 19.7 | -17.3 | -21.4 | -22.4 | -0.244 | -0.301 | -0.315 |
| 186885-4 | Unexposed | 102 | 234 | 15.4 | 25.4 | 195 | 12.3 | 19.0 | -16.5 | -20.1 | -25 | -0.162 | -0.197 | -0.245 |
| | | 39 | 93.6 | 15.6 | 2.67 | 98.1 | 15.2 | 2.7 | + 4.8 | - 2.5 | + 2.2 | +0.123 | -0.064 | -0.056 |
| | Exposed to 1 ppm $NH_3$ | 71 | 93.6 | 15.6 | 2.67 | 84.5 | 12.4 | 2.5 | - 9.7 | -20.5 | - 6.7 | -0.137 | -0.289 | -0.094 |
| 186880-1 | for 4 hrs. | 102 | 93.6 | 15.6 | 2.67 | 87.3 | 12.5 | 2.6 | - 6.7 | -19.8 | - 2.6 | -0.066 | -0.194 | -0.025 |
| | | 39 | 83.6 | 13.9 | 2.52 | 91.6 | 13.8 | 2.6 | + 9.5 | - 0.7 | + 4.3 | +0.244 | -0.018 | +0.110 |
| | Exposed to 1 ppm $NH_3$ | 71 | 83.6 | 13.9 | 2.52 | 77.9 | 11.3 | 2.4 | - 6.8 | -18.7 | - 4.8 | -0.096 | -0.263 | -0.067 |
| 186880-4 | for 4 hrs. | 102 | 83.6 | 13.9 | 2.52 | 82.2 | 11.8 | 2.5 | - 1.6 | -15.1 | - 0.79 | -0.016 | -0.148 | -0.008 |
| | | 38 | - | 15.9 | 25.2 | - | 12.3 | 18.6 | - | -22.4 | -26.1 | - | 0.589 | -0.687 |
| | | 70 | - | 15.9 | 25.2 | - | 10.7 | 17.9 | - | -32.5 | -29 | - | -0.464 | -0.414 |
| 186894-2 | Unexposed | 101 | - | 15.9 | 25.2 | - | 10.7 | 16.7 | - | -32.5 | -33.7 | - | -0.322 | -0.333 |
| | | 38 | - | 15.6 | 21.9 | - | 13.5 | 18.1 | - | -13.5 | -17. | - | -0.355 | -0.450 |
| | | 7) | - | 15.6 | 21.9 | - | 11.4 | 16.5 | - | -26.9 | -24.7 | - | -0.384 | -0.350 |
| 186894-3 | Unexposed | 101 | - | 15.6 | 21.9 | - | 12.3 | 16.4 | - | -21 | -25.1 | - | -0.208 | -0.249 |
| | | 38 | - | 12.4 | 1 | - | 12.1 | 1 | - | - 2 | 0 | - | -0.053 | 0 |
| | Exposed to 1 ppm $NH_3$ | 70 | - | 12.4 | 1 | - | 10.2 | 0.96 | - | -17.4 | - 4 | - | -0.249 | -0.057 |
| 186885-5 | for 40 min. | 101 | - | 12.4 | 1 | - | 10.4 | 0.99 | - | -15.8 | - 1 | - | -0.156 | 0.010 |
| | | 38 | - | 11.5 | 0.94 | - | 10.9 | 0.97 | - | - 5.2 | + 3 | - | -0.137 | +0.079 |
| | Exposed to 1 ppm $NH_3$ | 70 | - | 11.5 | 0.94 | - | 9.3 | 0.89 | - | -19.1 | - 5.3 | - | -0.273 | -0.076 |
| 186885-6 | for 40 min. | 101 | - | 11.5 | 0.94 | - | 9.1 | 0.84 | - | -20.8 | -10.6 | - | -0.206 | -0.105 |

TABLE 14. LONG TERM STABILITY OF PVA/NINHYDRIN COATED COLLECTOR/SENSORS

| Spec. No. | Specimen History | Elapsed Time, hrs. | Transmittance Readings: Initial White | Initial 5500nm | Final White | Final 5500nm | Percent Change in Transmittance: White | 5500nm |
|---|---|---|---|---|---|---|---|---|
| 186885-3 | Unexposed | 936 | 184 | 18.9 | 184 | 17.5 | 0.05 | - 7.4 |
| | | 1704 | 184 | 18.9 | 155 | 15 | -15.7 | -20.6 |
| 186885-4 | Unexposed | 936 | 234 | 25.4 | 232 | 23.6 | - 0.74 | - 7.1 |
| | | 1704 | 234 | 25.4 | 194 | 19.7 | -17.3 | -22.4 |
| 186880-1 | Exposed to 1 ppm $NH_3$ for 4 hrs. | 936 | 93.6 | 2.67 | 98.1 | 2.7 | + 4.80 | + 2.2 |
| | | 1704 | 93.6 | 2.67 | 84.5 | 2.5 | - 9.7 | - 6.7 |
| 186880 | Exposed to 1 ppm $NH_3$ for 4 hrs. | 936 | 83.6 | 2.52 | 91.6 | 2.6 | + 9.5 | + 4.3 |
| | | 1704 | 83.6 | 2.52 | 77.9 | 2.4 | - 6.8 | - 4.8 |
| 186894-2 | Unexposed | 912 | - | 25.2 | - | 18.6 | - | -26.1 |
| | | 1680 | - | 25.2 | - | 17.9 | - | -29 |
| 186894-3 | Unexposed | 912 | - | 21.9 | - | 18.1 | - | -17.1 |
| | | 1680 | - | 21.9 | - | 16.5 | - | -24.5 |
| 186885-5 | Exposed to 1 ppm $NH_3$ for 40 min. | 912 | - | 1 | - | 1 | - | 0 |
| | | 1680 | - | 1 | - | .96 | - | - 4 |
| 186885-6 | Exposed to 1 ppm $NH_3$ for 40 min. | 912 | - | .94 | - | .97 | - | + 3 |
| | | 1680 | - | .94 | - | .89 | - | - 5.3 |

The observed effects of initial decrease in transmission within several days after rod coating followed by good stability was also found to occur for the finalized mixed PVP/PVA polymer coating developed as the program neared completion. In fact, during the field testing portion of this program, this coating formulation was observed to provide enhanced stability over the PVP alone.

We speculate that the initial decrease in transmission, discussed above, may be due to the introduction of ammonia/ammonium compounds from handling and various sources of contamination and/or exposure of the water coating solutions to ambient concentration of ammonia at the time of coating of the rods.

Additional stability tests addressed the problem of assessing the effect of temperature upon stability, particularly in determining whether or not storage of the collector/sensors at sub-ambient temperatures might improve stability.

All specimens were stored in tightly closed one dram vials to protect them from the air. For this stability study, the temperature and humidity were kept constant. In addition to placing collector/sensors in a dark area at room temperature, two specimens were placed in a freezer at a temperature of -16°C. The results of this study are shown in Table 15.

TABLE 15. STABILITY COMPARISON OF POLYMER/NINHYDRIN COATED COLLECTOR/ SENSORS STORED AT AMBIENT AND SUB-AMBIENT TEMPERATURES

| Spec. No. | Polymer/Reagent | Temperature, °C | Elapsed Time(t) days | Transmittance Readings | | | | | | Δt,days | *Percent Change in Transmittance (ΔT) | | | Average Rate of Percent Change in Transmittance (ΔT/Δt),%/days) | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | | Initial | | | Final | | | | | | | | | |
| | | | | White | 550nm | 700nm | White | 550nm | 700nm | | White | 550nm | 700nm | White | 550nm | 700nm |
| 190101-4 | PVP/Ninhydrin | 25 | 8 | 239.5 | 28.7 | 12.6 | 232 | 27.3 | 12.3 | 8 | - 3.1 | - 4.9 | - 2.4 | - 0.4 | - 0.6 | - 0.3 |
| 190101-4 | PVP/Ninhydrin | 25 | 35.25 | 239.5 | 28.7 | 12.6 | 205.5 | 23.3 | 11.5 | 27.25 | -11.1 | -13.9 | - 6.3 | - 0.4 | - 0.5 | - 0.3 |
| 190101-4 | PVP/Ninhydrin | -16 | 69.25 | 239.5 | 28.7 | 12.6 | 211.5 | 23.5 | 11.65 | 34 | + 2.5 | + 0.7 | + 1.2 | -0.17 | - 0.26 | - 0.11 |
| 190101-5 | PVP/Ninhydrin | 25 | 8 | 224.5 | 26.8 | 11.2 | 211.5 | 24.8 | 10.9 | 8 | - 5.8 | - 7.3 | - 2.7 | - 0.7 | - 0.9 | - 0.33 |
| 190101-5 | PVP/Ninhydrin | 25 | 35.25 | 224.5 | 26.8 | 11.2 | 190 | 21.3 | 10.2 | 27.25 | - 9.6 | -13.2 | - 6.2 | - 0.44 | - 0.6 | - 0.3 |
| 190101-5 | PVP/Ninhydrin | 25 | 69.25 | 224.5 | 26.8 | 11.2 | 186.5 | 20.6 | 10.25 | 34 | - 1.6 | - 2.5 | - 0.4 | - 0.24 | - 0.33 | - 0.12 |
| 190103-4 | PVP/Ninhydrin | 25 | 8 | 281 | 33.6 | 12.8 | 269 | 31.8 | 12.8 | 8 | - 4.2 | - 5.5 | 0 | - 0.5 | - 0.7 | 0 |
| 190103-4 | PVP/Ninhydrin | 25 | 35.25 | 281 | 33.6 | 12.8 | 264 | 30.2 | 12.8 | 27.25 | - 1.8 | - 4.6 | 0 | - 0.2 | - 0.3 | 0 |
| 190103-4 | PVP/Ninhydrin | -16 | 69.25 | 281 | 33.6 | 12.8 | 265.5 | 30.55 | 12.3 | 34 | + 0.5 | + 1.1 | - 4 | - 0.08 | - 0.13 | - 0.06 |
| 190103-5 | PVP/Ninhydrin | 25 | 8 | 333.5 | 39.5 | 15.2 | 319.5 | 38.0 | 14.6 | 8 | - 4.2 | - 3.8 | - 3.9 | - 0.5 | - 0.48 | - 0.49 |
| 190103-5 | PVP/Ninhydrin | 25 | 35.25 | 333.5 | 39.5 | 15.2 | 308.5 | 36.2 | 14.5 | 27.25 | - 3.3 | - 4.6 | - 0.7 | - 0.2 | - 0.24 | - 0.13 |
| 190103-5 | PVP/Ninhydrin | 25 | 69.25 | 333.5 | 39.5 | 15.2 | 303.5 | 35 | 13.9 | 34 | - 1.5 | - 3.0 | - 3.9 | - 0.13 | - 0.16 | - 0.12 |

Note: All specimens were exposed to ammonia, measurements made using GLAD II.

*Represents percent changed in transmittance over the specified interval of time, Δt.

The transmittance values of those speciments stored at the lower temperature stabilized or increased only slightly whereas the transmittance values of those specimens stored at room temperature reflected a slight decrease. In either case, however, only minor changes in transmittance were observed. In some cases it may be desirable to store collector/sensors at low temperature when there is a long time interval between the initial measurement and actual exposure. However, additional studies should be made to verify this. The $\Delta\%\ T/\Delta t$, at both temperatures, shows a sharp decrease since the previous measurements, which is a good indication that the transmittance values have been stabilized for these collector/sensors.

4.8 EFFECT OF ROD LENGTH ON COLLECTOR/SENSOR SENSITIVITY

Exposure studies were made at the 1 ppm level using both 2 and 4 cm long quartz rods coated with PVA/ninhydrin. These studies showed the response was greater using the 4 cm rods. (See Figure 20). However, the effects on transmittance of coating degradation, such as surface scratches and humidity and other effects will also increase, as a rod length increases, thereby nullifying the beneficial effects of increasing rod length (Figure 21 shows this). In addition, the sensitivity using the 2 cm rods appears at this time to be adequate for measuring the low concentrations of ammonia ($\sim$30 ppb) in air. Consequently the 2 cm in length quartz rods were used during the remainder of

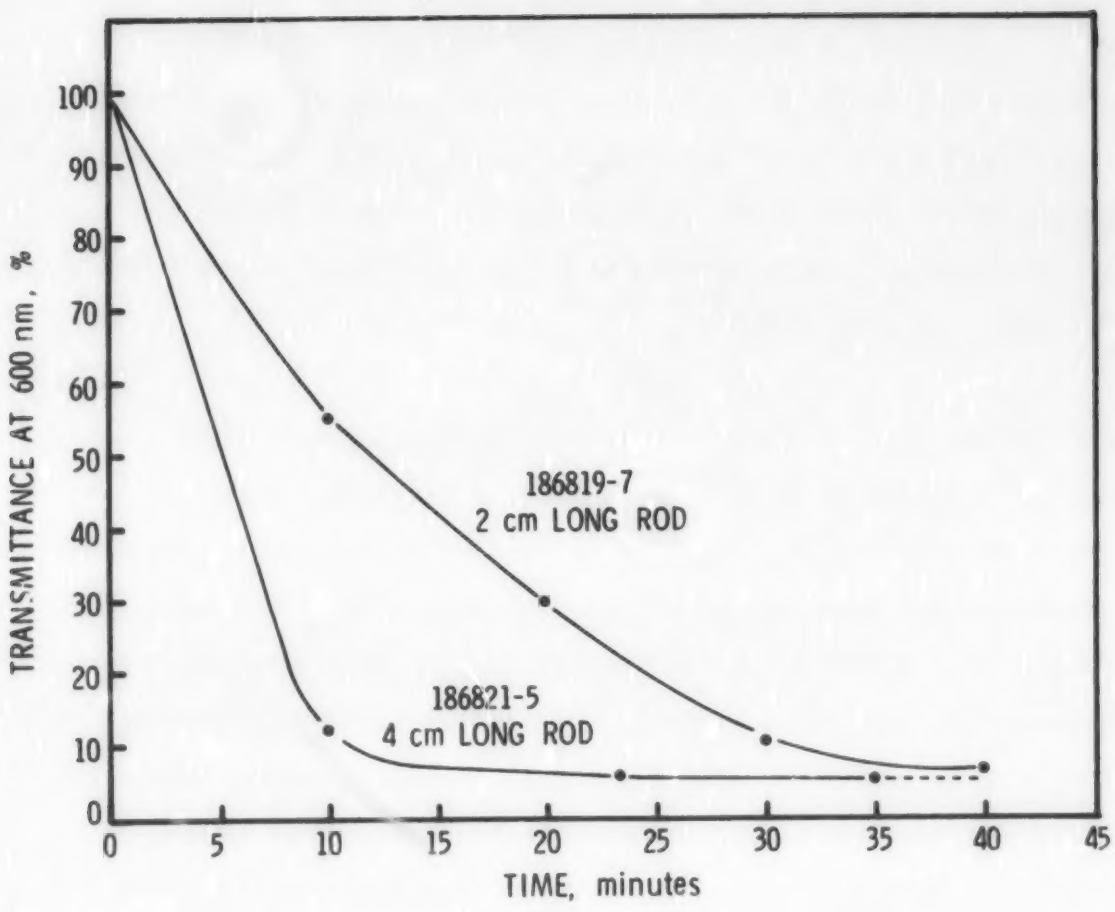



Figure 20. Effect of rod length on the transmission properties of coated rods exposed to 1 ppm ammonia in a saturated air stream

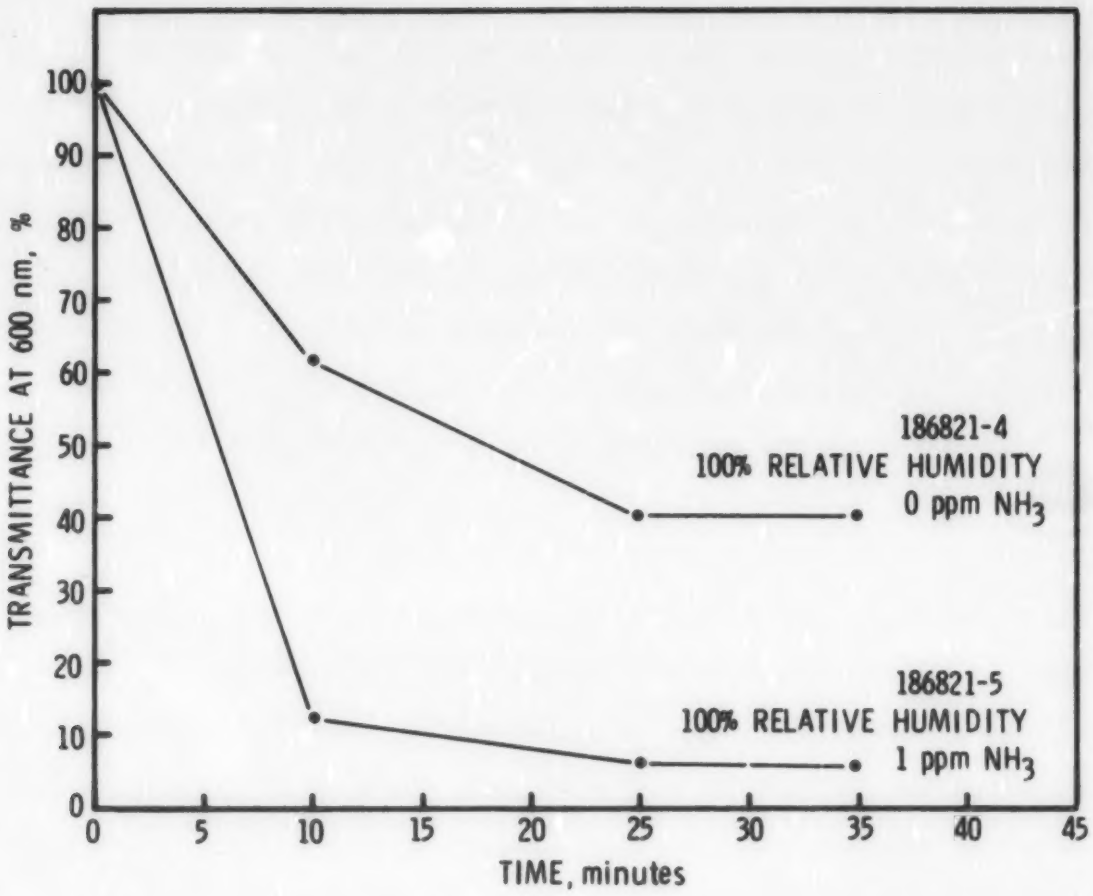



Figure 21. The effect of high humidity and/or ammonia concentration on 4 cm long PVA/ninhydrin coated rods exposed to 0 & 1 PPM ammonia in an air stream

the contract period.

## 4.9 EFFECT OF ACID POLLUTANTS AND AMMONIUM COMPOUNDS ON COLLECTOR/SENSOR RESPONSE

Using the experimental arrangement shown in Figure 22, specimens were exposed to either $SO_2$ or $NO_x$ in the presence of low concentrations of ammonia (60 ppb) in diluent air. The results of the study are shown in Figure 23. At high ppm levels of either pollutant an effect is observed on collector/sensor response. In the case of $SO_2$ the presence of the pollutant appeared to inhibit color formation. On the other hand an increase in response is observed with $NO_x$. However, at lower $SO_2$ or $NO_x$ levels (<0.5 ppm) little effect on collector/sensor response was noted.

During the initial qualitative screening reactions, we observed that ammonium compounds did indeed react with ninhydrin. However, differences in the color hue of the reaction product were observed between ammonia as such, and ammonium compounds. These observations are related to the total expected effect of interferants such as $SO_2$, $NO_x$, etc. since in addition to direct effects we might expect secondary effects due to the reaction with ammonia and formation of ammonium salts and subsequent reactions.

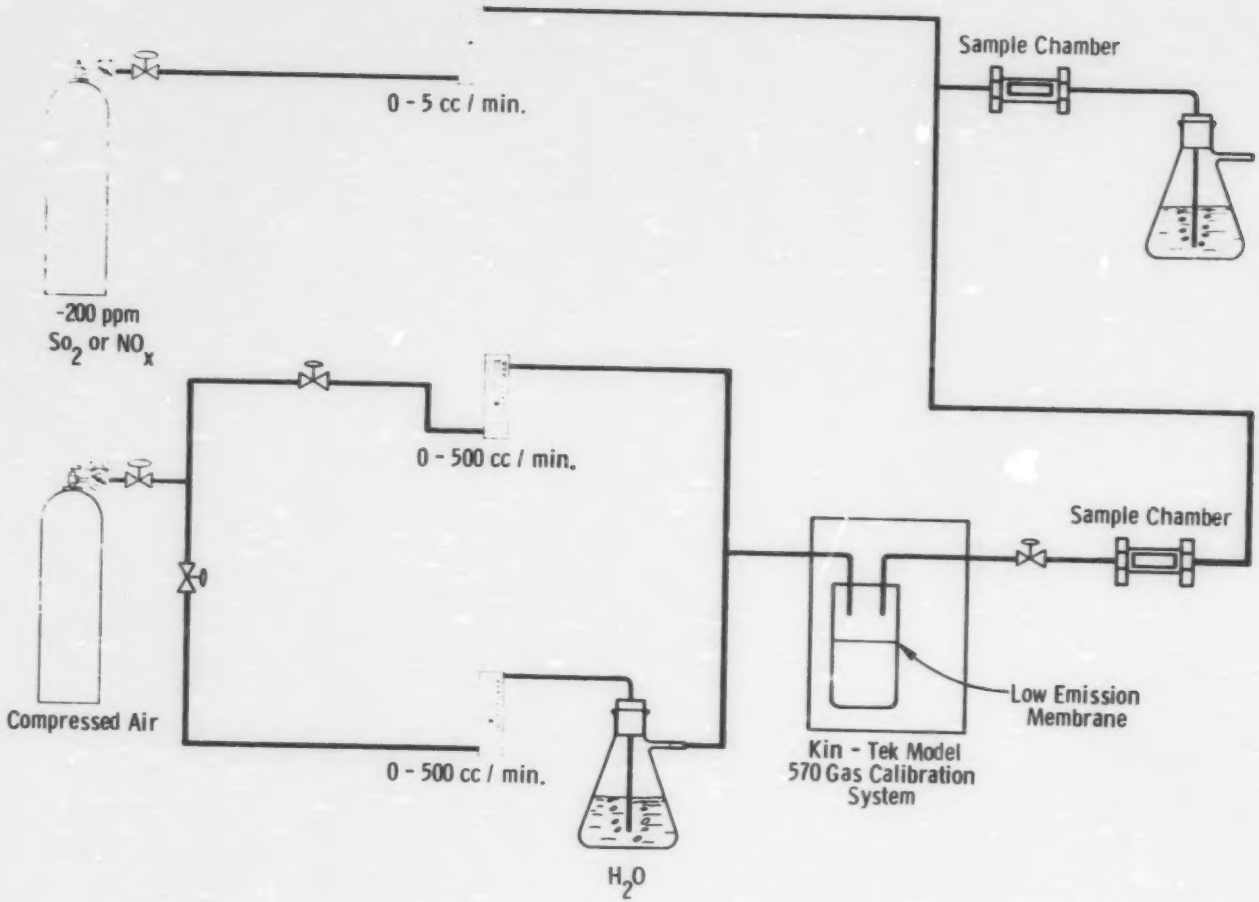



Figure 22. Schematic of apparatus used to simultaneously expose collector/sensors to acid pollutants and ammonia.

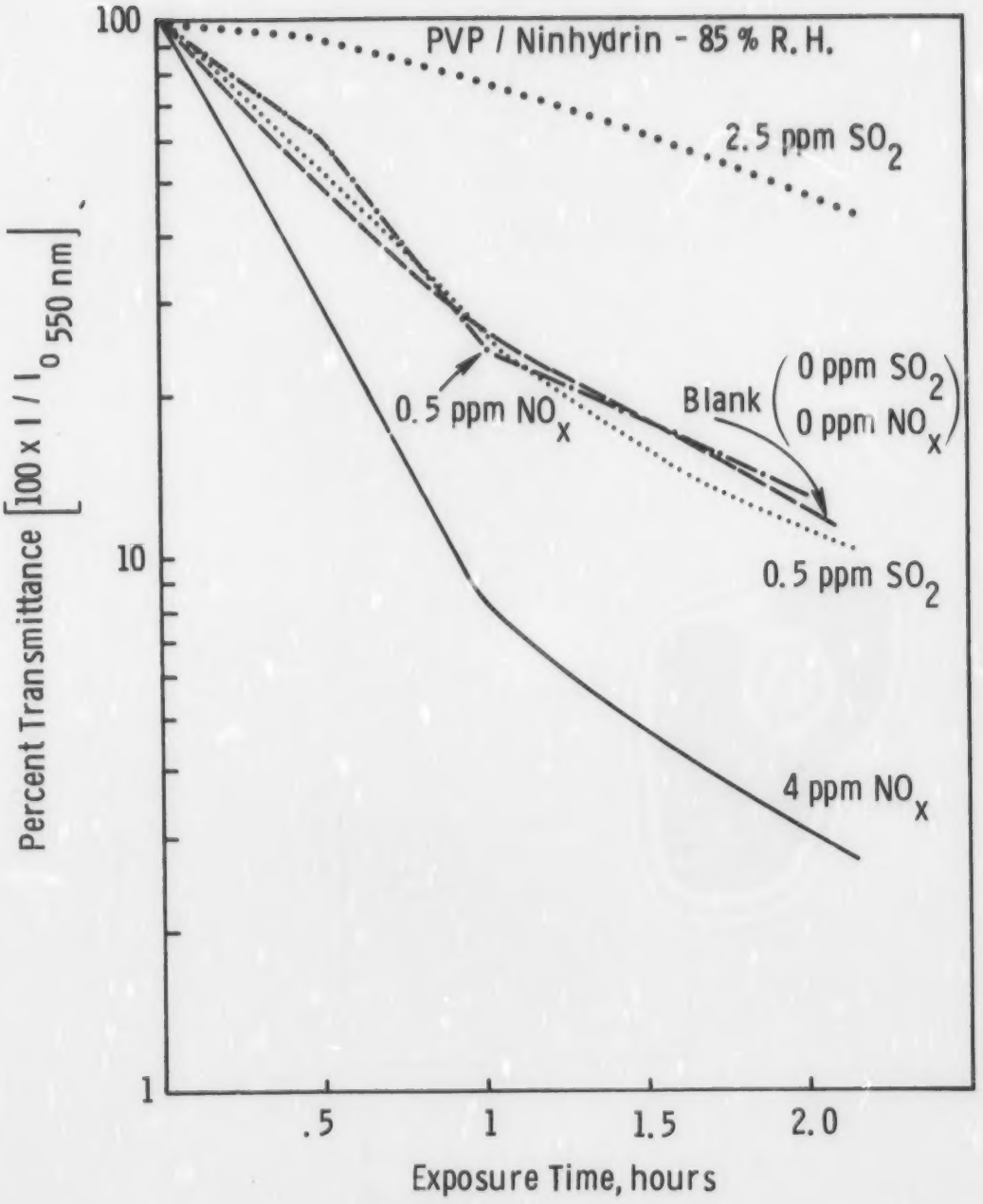



Figure 23. Effects of both acid pollutants and ammonia on the transmittance of PVP/ ninhydrin coated quartz rods.

We would normally expect the direct effects of $SO_2$ such as bleaching, inhibition of color formation, etc. along with the indirect effects of salt formation to lower the response. At approximately ten times the ambient concentration of $SO_2$ this is precisely what occurs whereas $NO_x$ has an opposite unexpected effect in that it increases the response. However, at the normally encountered atmospheric levels of $SO_2$ and $NO_x$, there appears to be a negligible effect from either pollutant at the 30 ppb level of ammonia.

It is interesting to note that at atmospheric levels of $SO_2$ and $NO_x$ (ppm) and ammonia (ppb) there was no effect on response even though $SO_2/NO_x$ were mixed in the vapor state and there was sufficient time for reaction with ammonia. This would seem to indicate that at the above concentration levels the presence of whatever concentration of ammonium salts/ammonium salt particulate that are formed have a negligible effect on the quantitative accuracy of the method.

## 4.10 EFFECT OF TEMPERATURE ON COLLECTOR/SENSOR RESPONSE

In order to maintain the PVP/ninhydrin collector/sensors at a specific temperature, a constant temperature water bath was used. Constant temperature was obtained by using the experimental arrangement shown in Figure 24 which made it possible for us to measure the response below room temperature. Specimens were exposed to 60 ppb $NH_3$ at 11°C and a relative humidity of 85%. Figure 25 shows the average transmittance as a function of exposure time for these studies. Previously, studies were made using similar exposure conditions at a temperature of 25°C and are also shown in Figure 25. The exposure studies at 11°C resulted in a greater response and higher sensitivity than was expected. The variation in collector/sensor response at these two temperatures is minimal and could very well be attributed to quartz or coating differences or to transmittance measurement errors. On the basis of these results any minor temperature variations encountered during collector/sensor exposure studies can be neglected.

The small effect of temperature on collector/sensor response observed here is contrary to that normally expected. The general effect of temperature and the anticipated effect here was discussed in a previous monthly report. This small temperature effect is probably due to the fact that this is a gaseous reaction and that the forward reaction rate constant is very large thus serving to minimize any temperature effects.

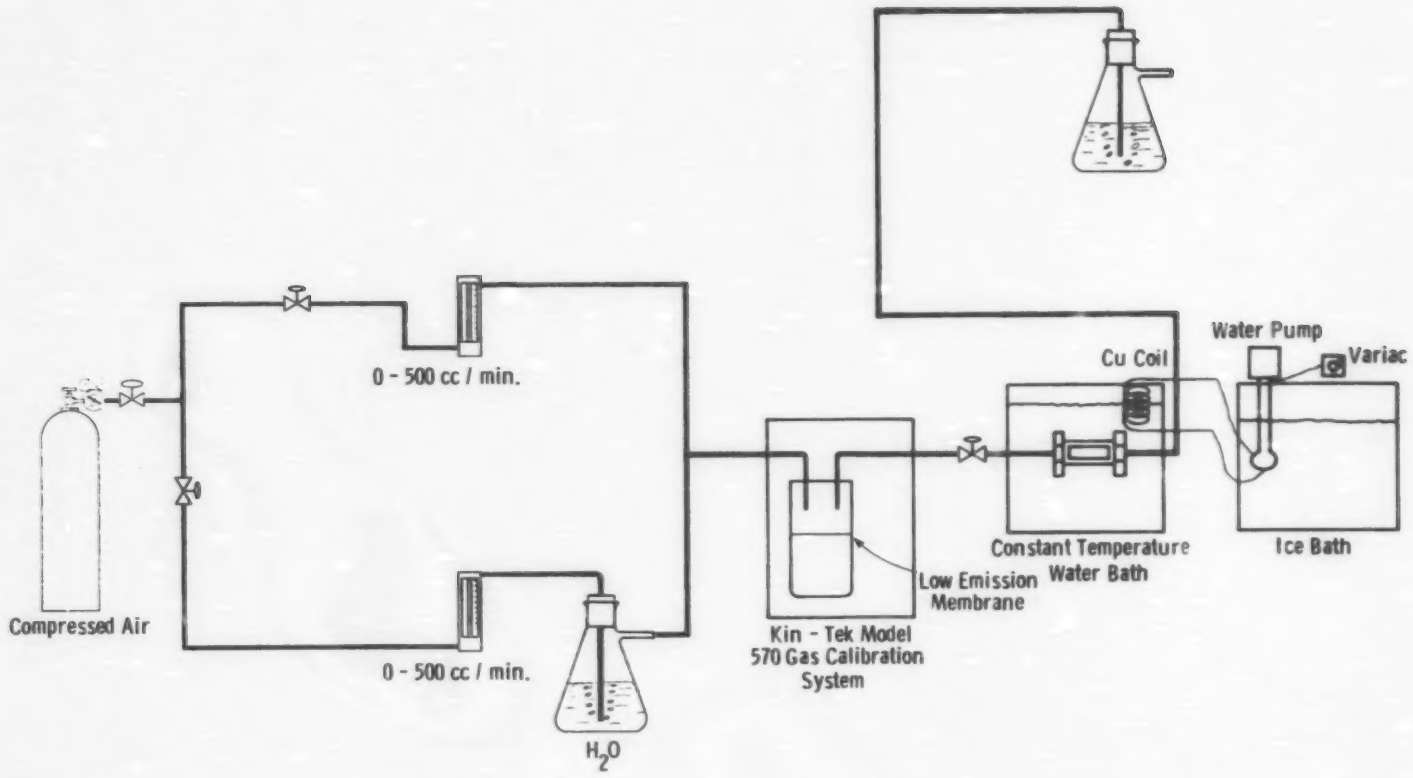



Figure 24. Schematic of apparatus used to expose collector/ sensors to ammonia at various temperatures

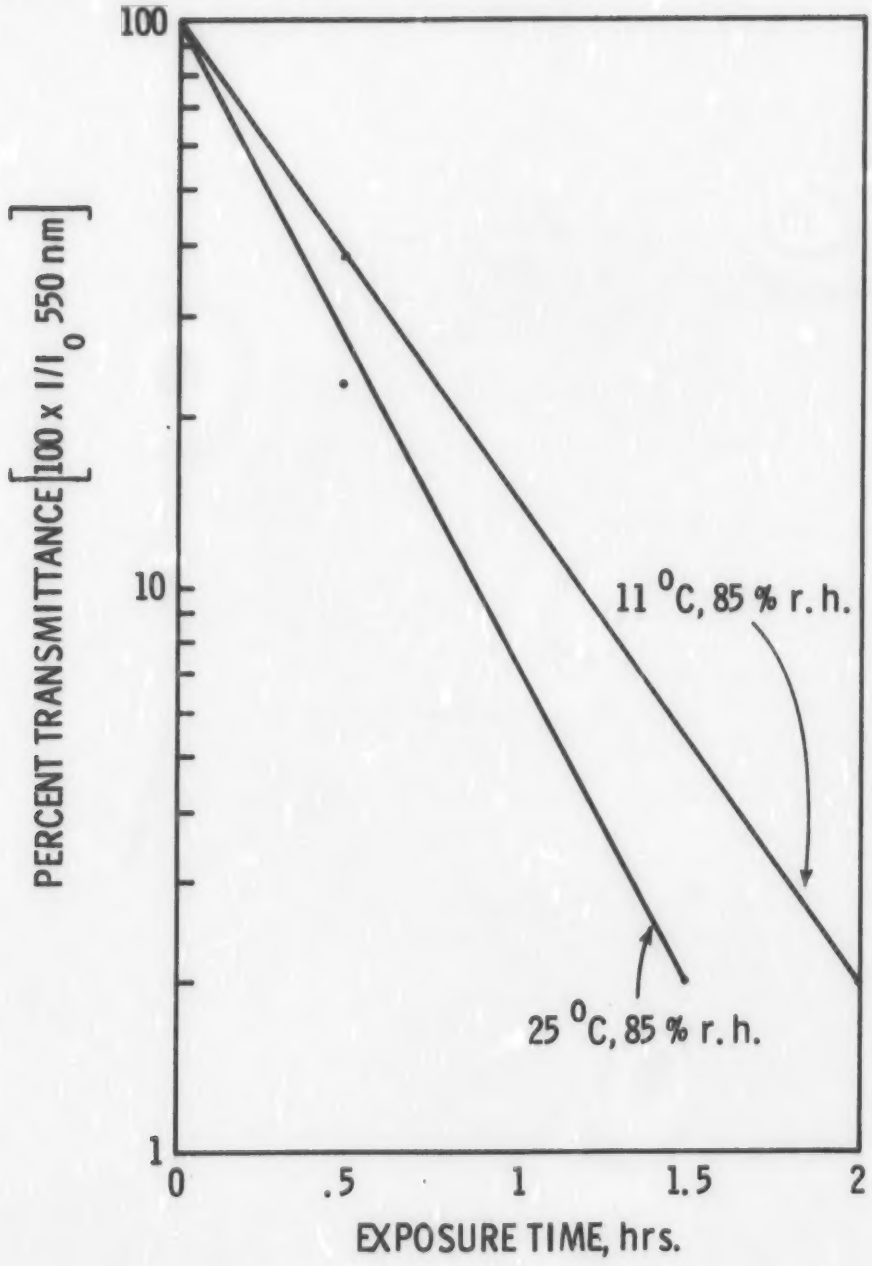



Figure 25. Effect of temperature and relative humidity on collector/sensors at 60 PPB ammonia level.

## 4.11 ABSORPTION WAVELENGTH

Based on transmission measurements made at various wavelengths throughout the visible spectrum, a maximum absorption wavelength of 550 nm has been employed for $NH_3$ measurements. These measurements were repeated using collector/sensors that had been coated with the finalized polymer coating which is a 50-50 mixture of PVP-PVA, ninhydrin which is buffered with potassium phthlate. Collector/sensors prepared in this manner and exposed to ammonia gave the curves shown in Figure 26. These curves show that the optimum wavelength of absorption is centered about 580 nm. Consequently, this wavelength should be used for measurements when this coating composition is used if maximum sensitivity is desired. The appropriate wavelengths of 550 nm or 580 nm were used for field measurements.

There appears to be an absorption peak near 400-450 nm. We speculate that this may be the result of small particles present in the coating of the collector/sensors which would scatter light at the shorter wavelengths and indicate an absorption peak as observed. We have observed that less sensitivity to changes in ammonia concentration and poorer reproducibility will be experienced if the lower wavelength is used. This is as expected because of the lower signal to noise ratio. High concentrations of $NH_3$ ($\gtrsim$50 ppm) and exposure to amines will tend to shift the wavelength of maximum absorption which should be redetermined under these conditions.

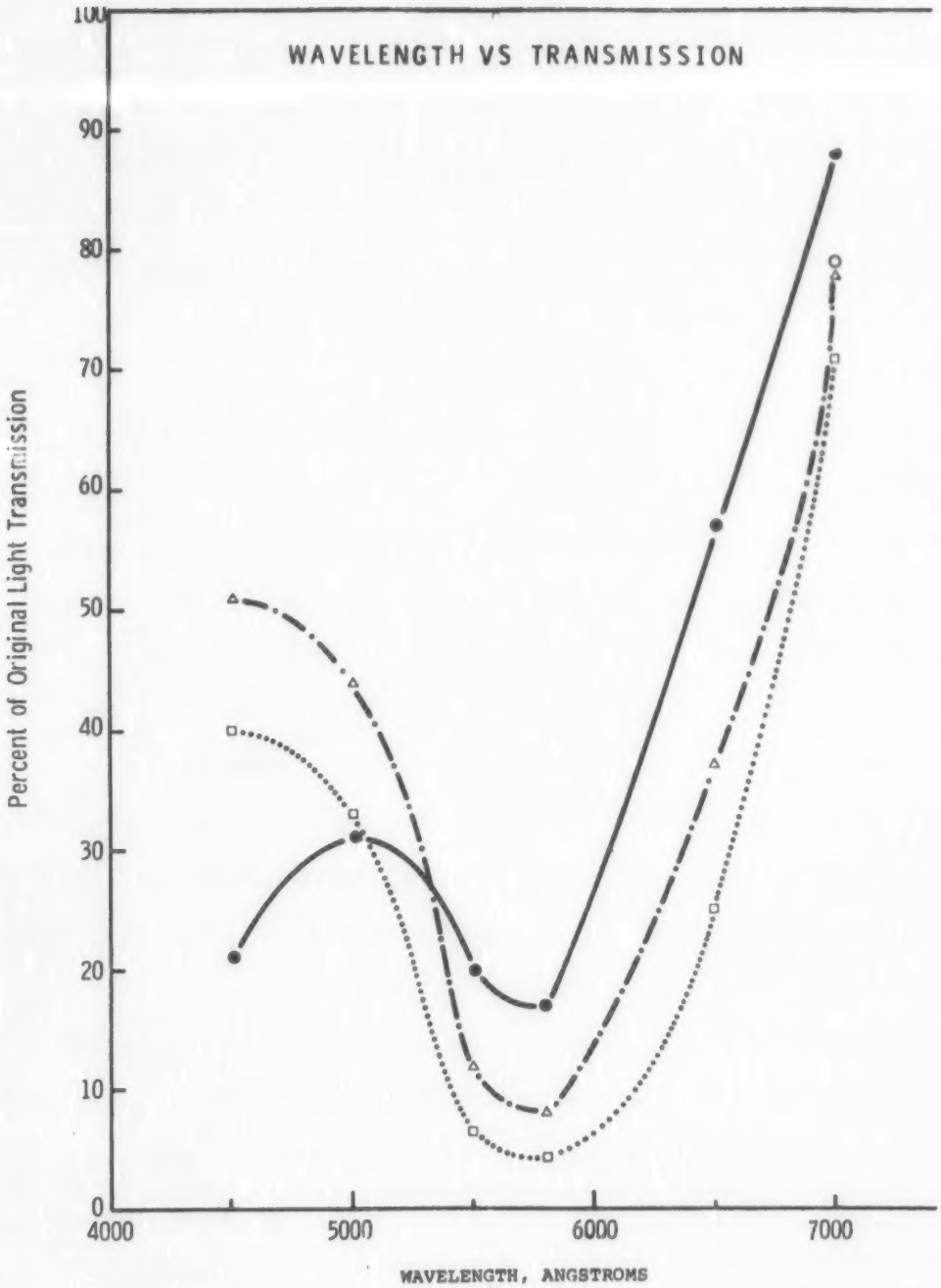



Figure 26. Absorption characteristics of reacted collector/sensors

## SECTION 5

## CALIBRATION

Calibration curves were obtained by exposing a number of collector/sensors from each batch to different ammonia levels for different exposure times. A typical calibration curve is shown in Figure 27. The transmittance (T) is defined as the final measured intensity (I) divided by the initial measured intensity ($I_o$) for a given exposure time. By plotting the product of ammonia concentration (c) and exposure time (t) only a single calibration curve is required. Calibration studies made at 0, 3, 30, 60, and 200 ppb $NH_3$ with the collector/sensors verifi-d the relationship between Absorbance (log 1/T) and c x t. This method then allows one to measure very low concentrations by increasing the exposure time. Using the calibration curve for an exposure time of 15 hours and a 1/T value of 7.3 the ammonia concentration would be 2 ppb.

This is the technique used for all subsequent ammonia measurements during this program including those made during the field testing. It should be noted that the blank response is quite low compared to the $NH_3$ response.

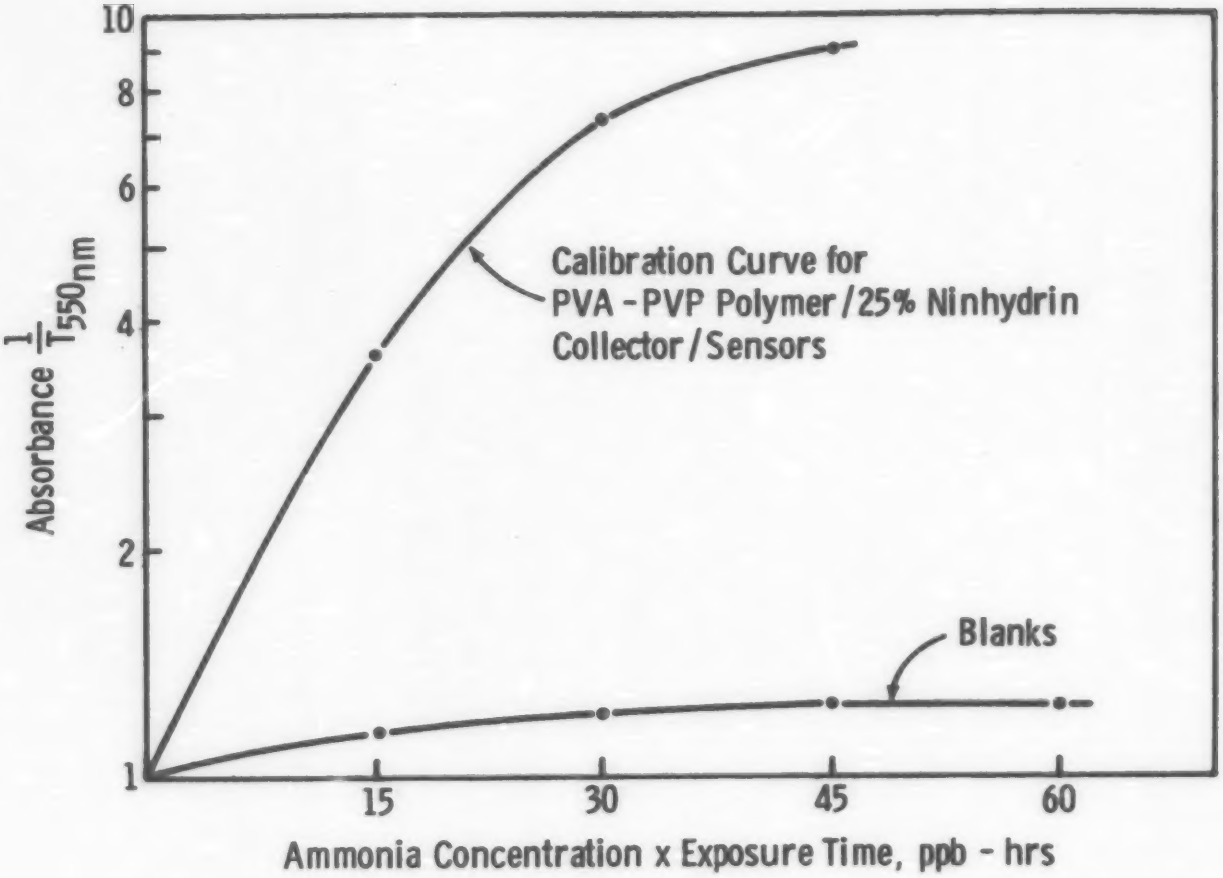



Figure 27. Effect of both ammonia concentration and exposure time on c/s absorbance

# SECTION 6

# RESULTS AND DISCUSSION

## 6.1 AMBIENT AIR MEASUREMENT OF $NH_3$ IN THE LABORATORY USING AN ARTIFICIAL HUMIDITY CHAMBER (HOLDER) AND DESIGN OF HOLDER

The possibility of utilizing an artificial humidity chamber has been investigated. A plastic perforated collector/sensor holder (humidor) was designed which houses a set of sponges. These sponges, soaked in distilled water, are placed in close proximity to the collector/sensors. A picture of the humidor is shown in Figure 28. Because th collector/sensor response depends, to an extent, upon relative humidity, we felt it should be possible to artificially provide adequate moisture in order to obtain sufficient measurement sensitivity. In-house studies at higher ammonia levels (0-10 ppm) were recently made which substantiate this. No significant difference in collector/sensor response was observed by varying relative humidity between 60% and 90% at an ammonia concentration of ∿8 ppm. The humidor alleviates the necessity of a high relative humidity by providing adequate moisture to the air immediately surrounding the collective-sensors. With this artificial source of moisture, the relative humidity of the surrounding air should be reduced to a secondary effect which would make it possible for exposure studies to be conducted over a wide range of humidity conditions.

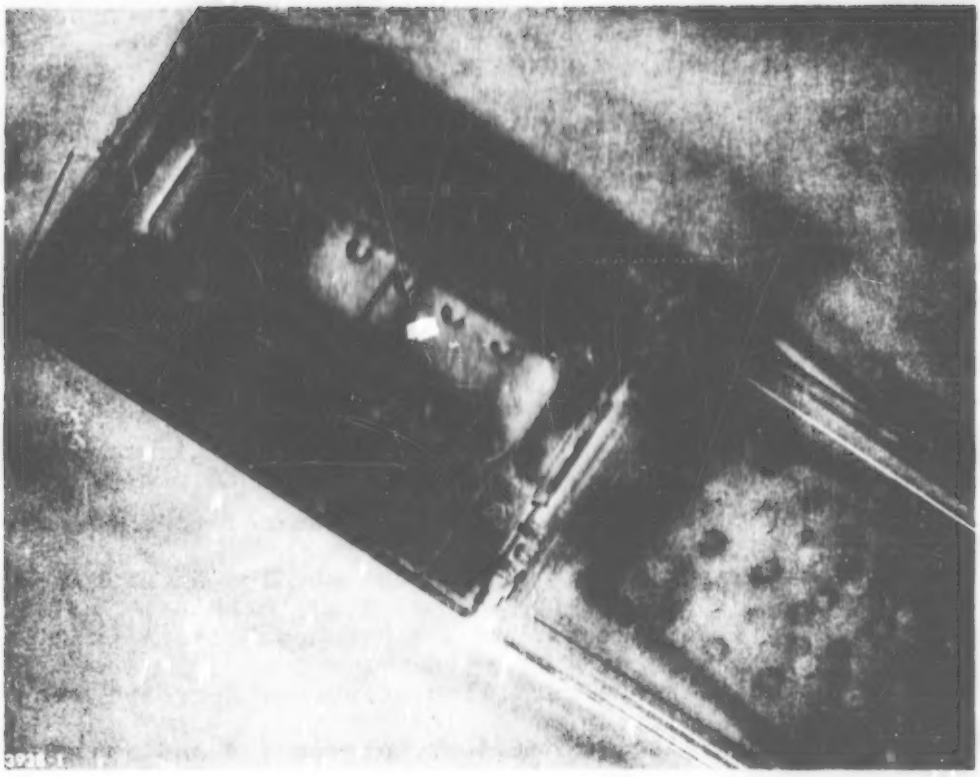


Figure 28. Artificial humidity chamber

In an effort to measure approximate ambient air ammonia concentrations in two separate laboratories, several collector/sensors were placed in a humidor and exposed to laboratory air. One set of collector/sensors were exposed in a laboratory with a constant relative humidity of 51% and a constant temperature of 24°C. A second set of collector/sensors were placed in an adjacent laboratory with a constant relative humidity of 20% and a temperature of 24°C. The results of these exposure studies are shown in Table 16. Collector/sensors were exposed for 25 hours in one case and 6 hours in the second. If we assume the relative humidity near the collector/sensor to be 85% in both cases, the ammonia concentration can be determined directly from the appropriate calibration curve. The exposure conditions and measured ammonia concentrations are also shown in Table 16.

Initial field testing was begun using the holder shown in Figure 28. In use, the holder was mounted in a High-Vol Sampler so that it was well-protected from direct wind currents. This protection was intended to prevent wind currents under changing conditions of humidity, from depleting the necessary moisture in the vicinity of the collector/sensors.

Under a separate in-house program, at higher concentrations of ammonia and large variations in wind velocity through the holder, we found that the effect of large changes in outside relative humidity (56-90) was to provide different calibration curves

TABLE 16. EXPOSURE CONDITIONS AND RESULTS OF COLLECTOR/ SENSORS EXPOSED TO AMBIENT AIR IN THE LABORATORY

| Spec. No. | 190146-7 | 190146-15 |
|---|---|---|
| Polymer/Reagent | PVP/Ninhydrin | PVP/Ninhydrin |
| Exposure Time, hrs. | 25.5 | 6.5 |
| Relative Humidity, % | 51 | 20 |
| Temperature, °C | 24 | 24 |
| Percent Transmittance, 550nm | 17 | 47 |
| *Concentration x Time | 41 | 17.5 |
| $NH_3$ Concentration, ppb | 1.6 | 2.7 |

with the holder shown in Figure 28. In order to minimize the effects of wind and large changes in relative humidity, the holder was modified to that shown in Figure 29. This design utilizes a double screen with 5 mil openings to cover the entire C/S opening which is the only entry into and out of the holder and thus prevents the free movement of air past the C/S. A wetted sponge extends across the area of the entire holder about 1/4" away from the C/S in order to insure the presence of moisture in the vicinity of the C/S. This holder was found to provide the same calibration curve for wide ranges of outside relative humidities thus obviating the necessity for any type of humidity correction.

## 6.2 FIELD TEST RESULTS

We felt it to be essential to have available a backup method that could be used to independently check the results the presnet GLAD technique under development. The problems associated with comparing GLAD results against a concurrent time integrated impinger sample are:

(1) At the ambient concentration of about 4 $\mu g/m^3$ (5.3 ppb) the GLAD responds in 4-6 hours whereas 500+ hours would be necessary for collection using a midget impinger at a nominal sampling rate in order to obtain sufficient quantity for analysis by classical methods.

(2) As a consequence of (1) different time periods will be involved making a comparison of the results difficult.

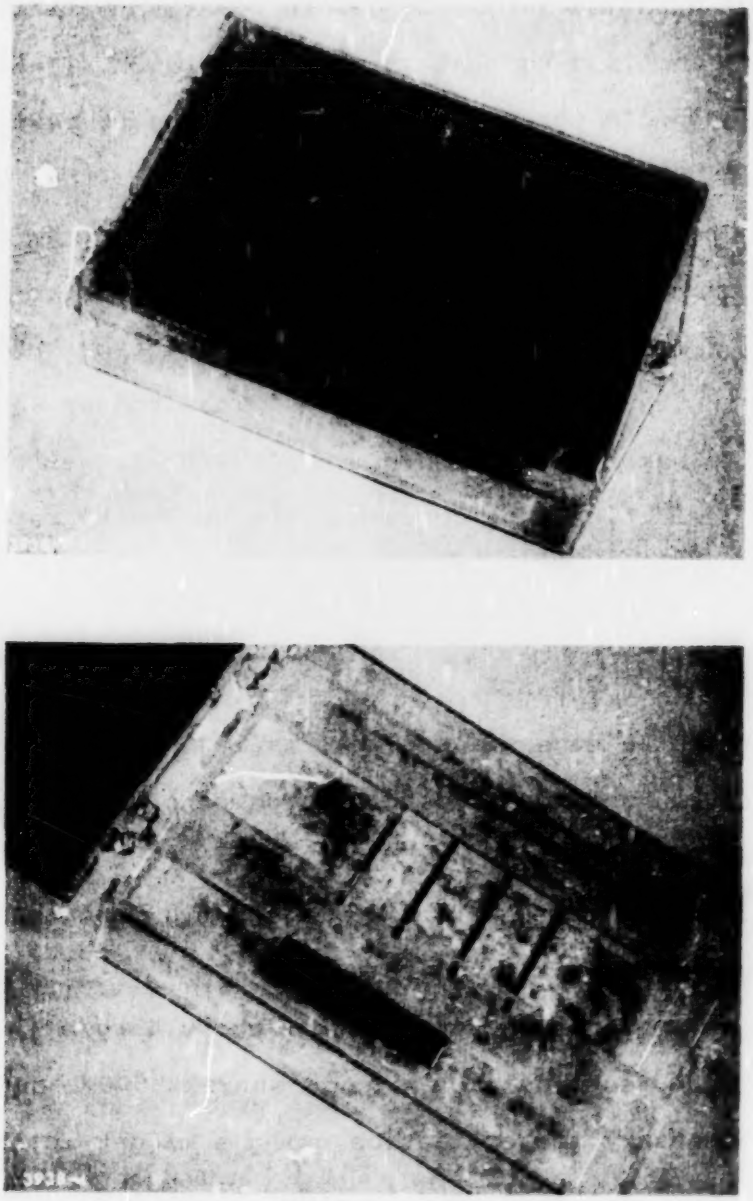


Figure 29. Modified G L A D C/S holder

(3) The effects of the atmospheric dirt, attendent interferences, recovery efficiencies and stability of the $NH_3$ species under long sampling times have not been classified.

The previous literature search showed that Okita and Kanomori[71] had developed analytical methodology that would provide an independent analytical check. This method utilizes a sulfuric acid impregnated glass fiber filter through which a large volume of air can be passed in a relatively short period of time to provide a sufficient mass of $NH_3$ for analysis. Due to time constraints, the effects of various experimental conditions on results were not rechecked and conditions as reported by Okita and Kanomori were utilized to provide the 95% - 98% collection efficiency that they reported. For the final analytical method, we used a water extraction of the filter which was subsequently analyzed by $NH_3$ specific ion electrode to provide the $NH_3$ concentration based upon the quality of air sampled.

Initial field testing of the C/S at the MRC Dayton Laboratory site began about July 9, 1976 using the polyvinyl pyrrolidone-ninhydrin coating formulation. An intrinsic objective of this effort was to determine whether or not correspondence between the backup analytical technique and the GLAD technique could be achieved.

---

[71]Okita, T. and Kanomori, S., Atmospheric Environment, 5, 621-627 (1971).

During some of the C/S exposure studies air was drawn through sulfuric acid impregnated glass fiber filters at a rate of 10-30 l/min in order to quantatively scrub the ammonia from the air. The $NH_3$ on the filter was subsequently extracted with water and the μg of $NH_3$/ml was determined with a specific ion electrode. It was not always possible to span the identical time period in which the C/S units were exposed but the filter sample results should be indicative of the ambient atmospheric ammonia concentration in the general time frame of C/S exposure. The results of the first Dayton site field testing are shown in Table 17.

The humidified effluent from the Kin-Tek permeation device which was used for calibrating the C/S was passed through an acid impregnated filter at a rate of 500 cc/min for twenty-two hours in order to serve as an accuracy check on the membrane permeation device. An analyzed value of 36.7 ppb vs. a calculated concentration of 30 ppb was obtained.

The collector/sensor holder shown previously in Figure 29 was positioned under the roof of an EPA Hi-Vol Sampler for protection from wind and rain as shown in Figure 30. In most cases the collector/sensors were exposed for 16 hours. Ammonia concentrations at the Dayton site over a three-week period were found to vary from <1 to 15 ppb with an average of 4.2 ppb for thirty-three separate measurements. Simultaneous parallel measurements were made in six tests using the method of Okita and Kanomori[71].

TABLE 17. ANALYTICAL RESULTS OF 1ST MRC DAYTON LABORATORY FIELD SITE TESTING

| Sampling Date | Location | R.H.% | Temp.°F | Formulation | $NH_3$ ppb Determined by GLAD | $NH_3$, ppb Determined From Filter |
|---|---|---|---|---|---|---|
| 7-9-76 | W | 53-62 | 72-78 | PVP | 6.2 | - |
| 7-9-76 | F | 53-62 | 72-78 | PVP | 6.1 | - |
| 7-13-76 | W | 49-54 | 71-77 | PVP | 5.7 | - |
| 7-13-76 | F | 49-54 | 71-77 | PVP | 5.3 | 6.4 |
| 7-22-76 | W | 97 | 79 | PVP | 7.6 | - |
| 7-22-76 | F | 97 | 79 | PVP | 8.0 | 12.8 |
| 7-26-76 | F | 40-91 | 85 | PVP | 5.0 | - |
| 7-26-76 | W | 40-91 | 85 | PVP | 14.9 | - |
| 7-28-76 | W | 59-78 | 75-85 | PVP | 7.3 | 3.9 |
| 7-29-76 | W | 67-74 | 83 | PVP | 14.8 | - |
| 7-29-76 | F | 67-74 | 83 | PVP | 5.0 | - |
| 8-2-76 | W | 42-55 | 69-73 | PVP | 4.1 | - |
| 8-2-76 | F | 42-55 | 69-73 | PVP | 6.1 | 3.1 |
| 8-3-76 | W | 47-70 | 61-66 | PVP | 5.1 | - |
| 8-3-76 | F | 47-70 | 61-66 | PVP | 2.1 | - |
| 8-3-76 | PCC | 47-70 | 61-66 | PVP | 1.3 | - |
| 8-4-76 | W | 63 | 60 | PVP | 2.8 | - |
| 8-4-76 | F | 63 | 60 | PVP | 2.3 | 3.5 |
| 8-5-76 | PCC | 88 | 65 | PVP | <1 | - |
| 8-6-76 | W | - | 69 | PVP | 5.2 | - |
| 8-6-76 | F | - | 69 | PVP | 3.7 | - |
| 8-6-76 | PCC | ~100 | 69 | PVP | <1 | - |
| 8-9-76 | F | - | - | PVP | <1 | <1 |
| 8-12-76 | F | - | - | PVP | 6.1 | - |
| 8-16-76 | F | - | - | PVA-PVP | <1 | - |
| 8-16-76 | F | - | - | PVP | <1 | - |
| 8-17-76 | F | - | - | PVP | <1 | - |
| 8-17-76 | F | - | - | PVA-PVP | <1 | - |
| 8-18-76 | F | - | - | PVA-PVP | 1.1 | - |
| 8-19-76 | L | - | - | PVA-PVP | 2.2 | - |
| 8-19-76 | L | - | - | | 1.1 | - |
| 8-24-76 | F | - | - | PVA-PVP | ~1.0 | - |
| 8-24-76 | F | - | - | PVP | <1 | - |

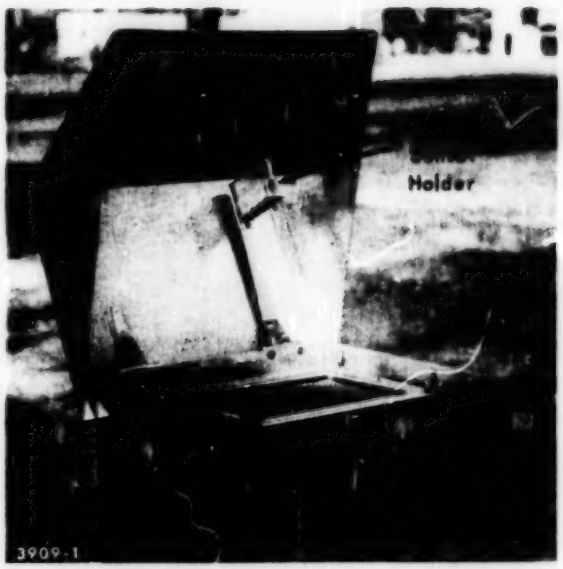



Figure 30. Holder in position under roof at high volume sampler

Sources of error in the filter analyses, particularly differences in the blank filters, appear to contribute approximately ±0.4 ppb uncertainty. Sulfuric acid impregnated filters held over approximately the same period of time as those used for the analyses were utilized as blanks. These analytical values obtained on these were used to correct the value obtained on the sample filters to correct for any $NH_3$ absorption during the period of transport and analysis.

Due to the humidity problem previously mentioned, and its effect on coating tackiness, we developed a second coating formulation during this part of the program which seems to largely overcome this problem. This was accomplished by using a 50-50 mixture of low molecular weight polyvinyl alcohol (PVA) and polyvinyl pyrrolidone (PVP). The PVA retains less moisture at the same relative humidity and provides the dimensional stability needed while the PVP comes to its equilibrium concentration of higher moisture level rapidly as before. Therefore, this combination provides both sensitivity and coating ruggedness. This coating formulation has also been found to provide improved initial stability as judged from the decrease in transmission (~2% average) during the first week after preparation. For these reasons this coating was used for the final field test at Dayton although the next set of field tests were made with both the PVP and 50% PVA/50% PVP formulations since previous field test results had been obtained using this formulation only near the completion of

tests and it was therefore necessary to test both formulations concurrently in order to identify any unanticipated problems.

Because of an EPA study being carried out at a St. Louis EPA Site (No. 108) and the apparent availability of one or more instrumental techniques at that time, Mr. J. Mulik, the contract monitor, suggested that our field tests be carried out at this location. This portion of the field testing effort was considered to be an important aspect of the program since it afforded an opportunity for a cross-check with one or more independent methods such as, chemiluminescent analyzer, laser diode infrared, or opto-acoustic infrared analyzer.

Field tests were begun at the EPA St. Louis Site No. 108 on August 18, 1976 using the holder shown in Figure 29. On the morning of August 21, 1976 at the St. Louis site, simultaneous analyses with the GLAD (integrated response) and the EPA-$NH_3$ chemiluminescent analyzer (real time response) were obtained. It appeared that there was generally good correspondence between the two techniques except for periods of time during the early morning hours that plumes came through the area which caused the chemiluminescent analyzer to register high peak concentrations of $NH_3$. An ammonia concentration of ~1 ppb was measured with the GLAD which checked the corresponding filter sample result. It was estimated that these results should have been on the order of 3-4 ppb in order to agree with the time weighted

average results (estimated) of the chemiluminescent analyzer. The plume presence was confirmed by laser diode and filter correlation spectrometers which monitored the presence of CO and NO. Additional $NH_3$ measuring instrumentation was not available at this time for cross-check analyses.

Dr. W. McClenny of the EPA subsequently found that the $NH_3$ chemiluminescent analyzer results were compromised by the presence of high concentrations of NO (confirmed by the other spectral methods mentioned) which was found to interfere with the chemiluminescent method and cause the chemiluminescent analyzer to produce high results in its present configuration.

Generally good agreement was observed with ammonia concentrations ranging from 1.1 ppb to 3.4 ppb with an average of 1.9 ppb using our technique. Measurements made simultaneously with the parallel method gave an average value of 1.1 ppb ammonia. Measurements at both sites showed the reproducibility to be ~±50% as opposed to ±10% observed in the lab. These results are shown in Table 18.

The concentrations of CO and $SO_2$ were tabulated in order to evaluate possible cross effects on the $NH_3$ concentrations measured. Although more measurements of all three materials are required before a conclusion can be reached, we can say that from the limited data available CO and $SO_2$ do not appear

TABLE 18. ANALYTICAL RESULTS OF ST. LOUIS FIELD SITE TESTING AT EPA REGIONAL AIR POLUTION SITE #108 IN VICINITY OF GRANITE CITY, ILLINOIS

| Sampling Date | Avg. R.H.,% | Avg. Temp.,°C | Formulation | $NH_3$ ppb Determined by Glad | $NH_3$ ppb Determined From Filter | CO, ppb | $SO_2$ ppb |
|---|---|---|---|---|---|---|---|
| 8-18-76 | 74 | 21.4 | PVA-PVP | 3.4 | 1.2 | 50 | 2.5 |
| 8-18-76 | 74 | 21.4 | PVP | <1 | 1.2 | 50 | 2.5 |
| 8-19-76 | 74 | 22.3 | PVA-PVP | 1.1 | ∿1 | 439 | 4 |
| 8-19-76 | 72 | 22.3 | PVP | <1 | ∿1 | 439 | 4 |
| 8-20-76 | 75 | 23.4 | PVA-PVP | 1.1 | ∿1 | 522 | 5 |
| 8-20-76 | 75 | 23.4 | PVP | <1 | ∿1 | 522 | 5 |
| 8-21-76 | 90 | 21.0 | PVA-PVP | <1 | <1 | - | 2.5 |
| 8-21-76 | 90 | 21.0 | PVP | <1 | <1 | - | 2.5 |
| 8-21-76 | 90 | 21.0 | PVA-PVP | <1 | <1 | - | 2.5 |
| 8-21-76 | 90 | 21.0 | PVP | <1 | <1 | - | 2.5 |

to be either positive or negative interferants to the ammonia measurements.

Additional measurements were made at the Dayton site using the new holder mentioned previously and shown in Figure 29 which was designed to maintain an essentially constant and high relative humidity. Also, a modified PVA/PVP polymer-ninhydrin coating formulation was prepared containing a buffer to control the pH at ∿ 4.5 during exposure. The addition of the buffer insures uniform color development and absorption at the same wavelength from batch to batch in spite of pH variation in the polymer, distilled water, and/or conditions of use.

Measurements made over a 16 hour exposure period using the improved holder and buffered coating gave a reproducibility of ±10%, even though the absolute values now being determined are about an order of magnitude below the original requested detection limit. Over an eleven-day period the ammonia concentration varied from <0.1 to 0.8 ppb. At these ranges the absolute values appear to be reasonable checks. Simultaneous measurements made using the filter collection method gave similar values. These results are shown in Table 19.

TABLE 19. ANALYTICAL RESULTS OF 2ND MRC DAYTON LABORATORY FIELD SITE TESTING USING IMPROVED HOLDER AND PVA/PVP COATING

| Sampling Date | Location | R.H. | Temp. °F | Formulation | $NH_3$ppb Determined by Glad | $NH_3$ppb Determined From Filter |
|---|---|---|---|---|---|---|
| | | | | | 0.6 | |
| 10/4/76 | F | | | PVA-PVP | 0.9 | 0.9 |
| | | | | | 0.6 | |
| 10/5/76 | F | | | PVA-PVP | 0.3 | 0.9 |
| | | | | | 0.3 | |
| | | | | | 0.3 | |
| 10/11/76 | F | | | PVA-PVP | 0.13 | <0.3 |
| | | | | | 0.3 | |
| | | | | | 0.3 | |
| | | | | | 0.3 | |
| 10/13/76 | F | | | PVA-PVP | 0.3 | ~0.3 |

## SECTION 7

## PROCEDURES

### 7.1 SOLUTION PREPARATION

1. Prepare an 11.8% by weight solution of PVA (Polyvinyl Alcohol, K & K Laboratories, Inc., Plainview, New York), using the following procedure: in a flask (500 ml or larger), heat 150 ml distilled $H_2O$ to 95°C. Add 20 g PVA and stir until all PVA particles are wet (∿30 seconds). Place stirring bar in solution and cover flask with aluminum foil. Immerse solution in a container of hot water and stir ∿2.5 hours with $H_2O$ maintained at 100°C. Resultant solution is clear. Store in a tightly closed container.

2. Prepare an 11.8% by weight solution of Type N-K90 PVP (GAF Corporation, 140 West 51st Street, New York, New York) using the following procedure: in a flask (500 ml or larger), heat 150 ml distilled $H_2O$ to 95°C. Add 20 g PVP and stir until all PVP particles are wet (∿30 seconds). Place stirring bar in solution and cover flask with aluminum foil. Immerse solution in a container of hot water and stir ∿1.5 hours with $H_2O$ maintained at 100°C. Resultant solution is clear. Store in a tightly closed container.

3. Prepare a 24.8% solution of ninhydrin (ICN Pharmaceuticals Inc., Life Sciences Group, Cleveland, Ohio) by using the following procedure: Heat 35 ml distilled water to 85°C. Remove from heat. Add 8.69 g ninhydrin and stir until complete dissolving occurs.

4. To prepare coating solution, add 75 ml PVP solution to 75 ml PVA solution and stir until combined. Add ninhydrin solution and stir. Store resultant solution in tightly closed container.

7.2 ROD COATING

1. Clean rods by immersing in chromerge solution for 5 minutes. If rods are coated, clean by boiling in $H_2O$ for 10 minutes or until coatings have dissolved, then immerse in chromerge solution for 5 minutes. Rinse twice in distilled water, once in isopropyl alcohol and end with a boiling isopropyl alcohol rinse. Remove rods from this solution with teflon coated tweezers and place on holding tray to dry. Place tray in desiccator.

2. With teflon coated tweezers, place rods in rod holder. Tighten each rod with screw driver, being careful that each rod is secure in holder. However, too much pressure on rod

end will cause breakage.

3. Suspend rod holder shown in Figure 6 (with rods securely in place from Fisher Payne Dip Coater. Immerse rods in solution while suspended, being careful not to let rod holder touch solution (~3/4 of rod should be immersed).

4. Remove rods from solution at 5 inches/minute using the Fisher Payne Dip Coater.

5. Suspend rod holder containing c/s from a lab stand. Place infrared lamp 5" (12.7 cm) from suspended rod holder and c/s. A 5" (15.2 cm) diameter aluminum foil reflector is placed 2" (5 cm) from the assembly opposite the heat source. A thermometer is placed parallel to the rod holder and c/s.

6. Turn infrared switch to "on" position. When thermometer reaches 130°F, turn lamp off and leave assembly suspended for 25 minutes.

7. Loosen screws and use tweezers to rotate each c/s 180°. Tighten screws.

8. Apply coating following steps 3 through 6.

9. Place dried, prepared, c/s in clean, labeled, tightly

closed vials.

10. When ready to use c/s, remove from vial carefully with tweezers and place lengthwise on a lint-free paper towel that is backed by a flat surface. With tweezers in one hand, hold c/s steady. With other hand, remove coating from circumferential ends with a sharp razor being careful not to damage ends of rod.

## 7.3 ANALYTICAL RESULTS

### 7.3.1 Collector/Sensor Exposure and Calculations

1. With teflon coated tweezers carefully remove unexposed c/s from vial and place in GLAD. Record transmission value at predetermined wavelengths (white light, 5800A° for ammonia).

2. Remove c/s, rotate 180°, place in GLAD and record transmission value.

3. Calculate the initial transmission value by taking the average of 1 & 2.

4. At the testing site, place unexposed c/s in humidor using teflon coated tweezers.

5. After exposure, open humidor at testing site and let c/s set ∿7 minutes before handling.

6. Remove c/s from humidor and carefully place in vials until transmission measurements are made.

7. Repeat steps 1 & 2.

8. To determine final transmission, take the average of the 2 transmission values recorded in step 7.

9. Determine the % transmission by dividing the final transmission by the initial transmission.

10. The concentration x time value is obtained from a calibration curve obtained in a similar manner using the 1/T value of the transmission change obtained in step 9.

11. Division by the time of exposure gives concentration directly.

## REFERENCES


1. Sittig, Marshall, "Pollution Detection and Measuring Handbook," Park Ridge, N. J., Noyes Data Corp. (1974).

2. Hardy, E. E., David, D. J., Kapany, N. S. and Unterleitner, F. C., *Nature* 257, 666 (1975).

3. David, D. J., Willson, M. C., and Ruffin, D. S., *Analytical Letters*, 9(4), 389 (1976).

4. Halasz, I., *Anal. Chem.* 36, 1429 (1964).

5. David, D. J., "Gas Chromatographic Detectors", *Wiley-Interscience*, New York (1974).

6. "Development of Instrumentation and Methodology to Measure Gaseous and Particulate Ammonia", MRC Proposal to E.P.A. No. P75-3D, 8 January 1975.

7. Makris, K. G., Z. *Anal. Chem.* 81, 212-4 (1930); *C.A.* 24, 4731 (1930).

8. Makris, K. G., Z. *Anal. Chem.* 84, 241-2 (1931); *C.A.* 25, 4200 (1931); Welcher, "Organic Analytical Reagents," Vol. II, D. Van Nostrand, New York, N. Y. 1974, p. 172.

9. Castellana, V., *Gazz Chim. Ital.* 36, 232 (1906); Welcher, "Organic Analytical Reagents," Vol. II, D. Van Nostrand, New York, N. Y. 1947, p. 173.

10. Korenman, I. M., Z. *Anal. Chem.* 90, 115-18 (1932); *C.A.* 27, 43 (1933); Welcher, "Organic Analytical Reagents," Vol. II, D. Van Nostrand, New York, N. Y., 1947, p. 323.

11. *Ibid.*, p. 409.

12. *Ibid.*, p. 416.

13. *Ibid.*, p. 423.

14. Koronman, I. M., *Z. Anal. Chem.* 90, 115-18 (1932); *C.A.* 27, 43 (1933); Welcher, "Organic Analytical Reagents", Vol. II, J. Van Nostrand, New York, N. Y., 1947, p. 438.

15. *Ibid.*, p. 458.

16. Feigl, F., *Mikrochemie* 13, 132 (1933); Feigl, F. "Spot Tests in Inorganic Analysis," 5th Edition, Elsevier Publishing, New York, N. Y. 1958, p. 237.

17. Zonghelis, C., *Compt Rend.* 173, 153 (1921); Feigl, F. Spot Tests in Inorganic Analysis", 5th Edition, Elsevier Publishing, New York, N. Y. 1958, p. 238.

18. Tananaeff, N. A. and Budkewitsch, A. A., *C.A.* 30, 5905 (1936); Feigl, F., "Spot Tests in Inorganic Analysis" Elsevier Publishing, New York, N. Y. 1958, p. 238.

19. Melissa, H., *Mikrochem. Ver. Michokim Acta* 38, 386 (1951); Feigl, F. "Spot Tests in Inorganic Analysis", Elsevier Publishing, New York, N. Y. 1958, p. 239.

20. Jonescu, A. and Harsovescu, C., *Bil. Soc. Chim. Romania* 4, 61-5 (1923); Welcher, "Organic Analytical Reagents" Vol. I, D. Van Nostrand, New York, N. Y., 1947, p. 104.

21. Foxwell, G. E., *Gas World* 64, No. 1654 (coking section) 10 (1916); *C.A.* 10, 1484, 1916; Welcher, "Organic Analytical Reagents", Vol. I, D. Van Nostrand, New York, N. Y. 1947, p. 149.

22. Caseneuve, A., *Bull. Soc. Pharm. Bordeaux* 61, 153-5 (1923); *C.A.* 18, 208 (1924); Welcher, "Organic Analytical Reagents, Vol. I, D. Van Nostrand, New York, N. Y., 1947, p. 181.

23. Lapin, L. and Hein, W., *Z. Anal. Chem.* 98, 236-40 (1934); *C.A.* 29, 78 (1935); Welcher, "Organic Analytical Reagents" Vol. I, D. Van Nostrand, New York, N. Y. 1947, p. 187.

24. Mangent and Marion, *Ann. Chim. Anal. Chim. Appli.* 8, 83 (1903); Welcher, "Organic Analytical Reagents", Vol. I, D. Van Nostrand, New York, N. Y., 1947, p. 240.

25. Duval, C., *Compt Rend.* 211, 588-90 (1940); *C.A.* 36, 365 (1942); Welcher, "Organic Analytical Reagents", Vol. I, D. Van Nostrand, New York, N. Y. 1947, p. 376.

26. Schoeller, W. R., *Analyst.* 57, 750-6 (1932); Welcher, "Organic Analytical Reagents", Vol. II, D. Van Nostrand, New York, N. Y. 1947, p. 172.

27. Reigler, R., *Chem-Ztg.* 21, Repertorium 307 (1897); Feigl, F., "Spot Tests in Inorganic Analysis", 5th Edition, Elsevier Publishing, New York, N. Y. 1958, p. 235-6.

28. Thomas, P., *Bull. Soc. Chim.* 11, 796-9 (1912); *C.A.* 6, 3241 (1912); Welcher, "Organic Analytical Reagents", Vol. I, D. Van Nostrand, New York, N. Y. 1947, p. 149.

29. Rosenthaler, L. *Microchemie* 13, 317 (1933); Wenger, P. and Duckert, R., "Reagents for Qualitative Inorganic Analysis", Elsevier Publishing Co., New York, N. Y. 1948, p. 245.

30. Wenger, P. and Duckert, R., "Reagents for Qualitative Inorganic Analysis", Elsevier Publishing Co., New York, N. Y., 1948, p. 248.

31. Crismer, R., *Bull. Soc. Chim. Biol.* 19, 1000 (1937).

32. Bolleter, W., Bushman, C., and Tidwell, P., *Anal. Chem.* 33(4), 592-594 (1961).

33. Williams, D. and Miller, R., *Anal. Chem.* 34(2), 225-227 (1962).

34. Benesch, R., *Helgolaender Wiss Meersunters* 23(3), 365-75 (1972); *C.A.* 78, 33725d (1973).

35. Bulusek, Jaroslau, *Sb. Ved. Pr. Vys. Sk. Chemickotechnol Paraducbice* 30, 141-59 (1973); *C.A.* 82, 38278c (1975)

36. Steinbrecher, K., *J. Assoc. Off. Anal. Chem.* 56(3), 598-601 (1973); *C.A.* 79, 41005e (1973).

37. Hegedus-Wein, Lldiko and Szam, Instran, *Orv Hetil* 114(43), 2614-15 (1973); *C.A.* 80, 142629n (1974).

38. Vchida, Tadashi, *Eisei Kinsa* 23(11), 868-70 (1974); *C.A.* 82, 12155f (1975).

39. Matsunaga, Katsuhiko, *Anal. Chim. Acta* 73(1), 204-8 (1974); *C.A.* 82, 64218c (1975).

40. Yamaguchi, Ryoji, *Hoshi Yakka Daigaku Kiyo* 14, 98-102 (1972); *C.A.* 78, 146982d (1973).

41. Hegedus-Wein, Ildiko, *Ber. Ges. Inn. Med.* D.D.R. 8, 241-2 (1972); *C.A.* 79, 29182c (1973).

42. Letkina, N. P. and Gurevich, T., *Sh. Zdravookhr Belarusa* 19(1), 32-4 (1973); *C.A.* 79, 2261r (1973).

43. Collins, P. F., *Beitr. Tabdkforsch* 6(4), 167-72 (1972); *C.A.* 78, 133602e (1973).

44. Suzuki, Kazuo, *Chomi Kagaku* 19(10), 23-6 (1972); *C.A.* 80, 144436w (1974).

45. Naito, Mariko and Vete, Tetsuo, *Kitano Byoin Kiyo*, 16(3-4), 102-6 (1971); *C.A.* 77, 72204g (1972).

46. Hasashiro, Hideto, *Rinshokensa* 18(6), 655-8 (1974); *C.A.* 82, 13307y (1975).

47. Ozkan, Kemal, *Ankard Univ. Tip. Fak, Mecm.* 25(5), 1011-22 (1972); *C.A.* 79, 63318m (1973).

48. Hegedus-Wein, I., *Med Welt*, 24 (31-32), 1205-7 (1973); *C.A.* 79, 102263m (1973).

49. Nikolin, B., *Tob Sci.* 18, 102-6 (1974); *C.A.* 80, 130645b (1974).

50. Okita, T. and Kanamori, I., *Atmos. Environ.* 5(8), 621-7 (1971); *C.A.* 75, 112608 (1971).

51. Truesdale, V., *Analyst* 96 (1145), 584-90 (1971); *C.A.* 75, 143863t (1971).

52. Chapman, B., Cooke, G. H., Whitehead, R., *Water Pollution Contr.* 66(2), 185-9 (1969); *C.A.* 71, 94633z (1969).

53. Kramer, D., Sech, J., U. S. Government Research and Development Dept., AD No. 713556, 12 pgs (1969); *C.A.* 75, 145805 (1971).

54. Rosenthaler, L., *Z. Anal. Chem.* 183, 193-4 (1961); *C.A.* 59, 28741 (1960).

55. Weller, H., *Roentgen-Lab Praxis* 15, L77-L85 (1962); *C.A.* 57, 10135 (1957).

56. Magill, Paul L., *Am. Ind. Hyg. Assoc. Quart.* 11, 55-63 (1950); *C.A.* 45, 2612f (1951).

57. Lugg, G. A. and Wright, A.S., Australia, Dept. Supply, Defence Research Labs., Circ. No. 14, 1-48 (1953); *C.A.* 47, 9857e (1953).

58. Vasilchenko, L. A. and Drozdova, V. M., *Fr. Gl. Geofiz. Observ.* No. 141, 99-103 (1963); *C.A.* 61, 1260g (1964).

59. Whitaker, J. R., *et al.*, *Clin. Chim. Acta* 12(4), 466-8 (1965); *C.A.* 63, 15212e (1965).

60. Levitski, A., *Anal Biochem.* 33(2), 335-40 (1970); *C.A.* 72, 87070f (1970).

61. Muramatsu, K., *Agr. Biol. Chem.* 31(3), 301-8 (1967); *C.A.* 67, 18468b (1967).

62. Newell, B. S., *J. Mar. Biol. Assoc. U. K.* 47(2), 271-80 (1967); *C.A.* 67, 85722f (1967).

63. Kudeyarev, U. N., *Agrokhimiya* 4, 129-34, (1966); *C.A.* 65, 4582a (1966).

64. Sojecki, Wojciech, *Pr. Cent. Inst. Ochr. Pr.* 17 (54), 213-23 (1967); *C.A.* 68, 5991n (1968).

65. Zverev, Yus, *et al.*, *Uses. Nauch.-Issled. Inst. Okhr. Tr.* 264-74 (1967); *C.A.* 70, 99375f (1969).

66. Kurczatowa, G., *Rocz. Panstw. Zakl. Hig.* 22(3), 289-94 (1971); *C.A.* 75, 91080p (1971).

67. Someya, Takeshi, Oshawa, Shigeki, *Nippon Kagaku Kaishi* (4), 744-747, 1972; *C.A.* 77, 42813n (1972).

68. Matsunaga, Katsuhiko, *Bunseki Kagaku* 20(8), 993-7, (1971); *C.A.* 76, 131258g (1972).

69. Janowski, Tomasz M., Zychlinski, Jozef, *Med Wet.* 25(10), 617-20, (1969); *C.A.* 72, 124794t (1970).

70. Deckert, W., *Z. Anal. Chem.* 150, 421-5, (1956); *C.A.* 50, 10607 (1956).

71. Okita, T. and Kanamori, S, "Atmospheric Environment", 5, 621-627 (1971).